THE REDUCED–EXPANDED SPACE METHOD
APPLIED TO ELECTRONIC SPECTROSCOPY

By

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To Alice

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THE REDUCED-EXPANDED SPACE METHOD APPLIED TO ELECTRONIC SPECTROSCOPY

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We describe a simple expansion of the Krylov type for the estimation of the electronic correlation energy of the ground state of closed-shell systems and show its relationship with Brillouin-Wigner Perturbation Theory. We demonstrate that Brillouin-Wigner Perturbation Theory can be quickly solved in a non-iterative fashion.

Examples are presented using Intermediate Neglect of the Differential Overlap Model Hamiltonian (INDO/1) which indicates that this scheme captures well over 95% of the correlation energy captured by the Configuration Interaction over double excitations method (CID) in a fraction of the computational effort.

We also described a generalization of the ground state method to obtain electronic spectra as a single excitation on top of the ground state Krylov-type expansion, with coefficients determined variationally. This results in a modified

Configuration Interaction over single excitations method (CIS) expanded with an average over doubles and triple excitations.

Examples are presented using Intermediate Neglect of the Differential Overlap Model Hamiltonian (INDO/1) which indicates that this scheme is competitive for transition energies and moments when compared with the much more demanding Configuration Interaction over all excitations method (CI Full)

We also investigated time independent response of a wavefunction constructed as a Configuration Interaction over singles (CI S) using the first order Rayleigh Schroedinger wave function as the reference and find that the results for dipole moment and polarizabilities are very encouraging

CHAPTER 1
INTRODUCTION

Motivation

Much effort has been and is being expended to obtain the Potential Energy Surfaces (PES) of molecular systems as a function of the nuclear coordinates. The interest in the calculation of Potential Energy Surfaces is rooted in

i The solution of the Electronic Hamiltonian for certain nuclear configurations which means the calculation of the potential generated by the electrons for the nuclear motion, is a well-defined problem.

ii It is a starting point for the understanding of a large variety of problems, e.g. structure, dynamics and spectroscopy, and thus of all chemistry.

Here we will concentrate on applications to electronic spectroscopy, photochemistry, and time-independent ground state properties. So we are interested not only in good transition energies, but also in reliable wave functions and the PES for the states of interest.

Section 3 of this chapter presents the Electronic Hamiltonian we are attempting to solve; section 4 shows the second quantized tools we used to derive our equations.

In chapter 2 we review some of the approximations to solve the Electronic Hamiltonian. We point out that within the Spin Symmetry Adapted Coupled Cluster we differ from Nakatsuji's work [1–18] by keeping the energy evaluation consistent through second order For closed-shell systems, we develop diagrammatic rules to obtain all the expressions over molecular orbitals instead of the usual ones over spin orbitals

In chapter 3 we analyze a Krylov like expansion for a closed-shell ground state We show that this expansion is closely related to a perturbation-variational treatment with respect to Brillouin-Wigner Perturbation Theory (BWPT) This development differs from other perturbation-variational methods (e.g. the one by Bartlett and Brändas [19–23]) as it does not use an expansion over positive powers of the Hamiltonian We develop a scheme that uses a power series in the denominator which forces a fast convergence of the perturbation series Rather we show the relationship between this expansion and BWPT and also introduce a non-iterative method to obtain Brillouin-Wigner energies

In chapter 4 we propose a method closely related to configuration Interaction over single excitations (CI S) for the calculation of polarizabilities, which we call Modified CI-S. This techniqueallows for orbital relaxation through the inclusion of single excitations on a correlated 1st order Rayleigh-Schroedinger wavefunction

In chapter 5 we Introduce our approximated method for electronic spec troscopy that we call Reduced Expanded Space. We try to incorporate the same level of correlation captured by a ground state 1st order Rayleigh Schroedinger wavefunction to the single excited states.

Finally, in chapter 6, we summarize our preliminary results.

History

In 1927, Heitler and London [24] performed the first quantum mechanical calculation on a molecular system, namely the hydrogen molecule. This paper marks the beginning of Quantum Chemistry. Theirs was a simple valence-bond type of calculation.

Much of what is done in this thesis though, does not use the valence bond approach or its generalizations [25, 26] but is rooted in the Self Consistent Molecular Orbitals method, which can be traced to the ideas of Hartree and Fock [27–30], and later to Roothaan [31, 32], and the molecular orbital picture of Hund [33] and Mulliken [34–37].

Actually, the first quantum mechanical calculation of Heitler and London was a correlated calculation as defined nowadays, i.e. correlation energy is the difference between the Hartree Fock limit and the exact nonrelativistic result. But one can trace to Møller and Plesset [38] the first attempt to directly obtain the correlation energy. Perturbation Theory was later more elegantly developed by Breuckner and Goldstone [39, 40].

Löwdin's papers [41, 42] provided an elegant way to interpret the increasingly more sophisticate methods like Configuration Interaction (CI) [43–48], Unrestricted Hartree Fock (UHF) [49] Multi Configuration Self Consistent Field (MC SCF) [50, 51], Coupled-Cluster Theory (CC) [52, 53] and methods based on the Equations Of Motion (EOM) [54–57]

By the late 1960's not only were transition energies and total energies being examined but efforts to calculate molecular properties had intensified [58–61] Coupled-Perturbed methods based on, for example Hartree Fock started to receive attention [62–64]

At the present, the effort continues to obtain more accurate properties and Potential Energy Surfaces for larger and chemically more interesting molecules

In this introduction, I do not make any distinction between ab-initio (all integrals are calculate from first principles) and semi-empirical calculations (some or all integrals are approximated), because in this thesis I consider all Hamiltonians in second- quantized form [65], and the formalism developed are identical.

The Electronic Hamiltonian from the Molecular Hamiltonian

The Born-Oppenheimer Approximation

The Born-Oppenheimer Approximation (BOA) [66–68] is based on the small mass of the electron relative to the nuclear mass, which allows the electrons to adjust instantaneously to the nuclear motion Hence the interaction between nuclei and electrons is a function of nuclear positions only. Thus electronic motion produces an effective potential for the nuclear motion.

The classical nonrelativistic Lagrangian of a field-free molecular system is

$$L = T - V \tag{1}$$

where, in atomic units, the Kinetic and Potential energies are written as

$$T = \frac{1}{2}\sum_{K=0}^{N-1} m_K \mathcal{R}_K^2 + \frac{1}{2}\sum_{i=1}^{n} \mathcal{R}_i^2 \tag{2}$$

$$V = \frac{1}{2}\sum_{K \neq L} \frac{Z_K Z_L}{\mathcal{R}_{KL}} - \sum_{K,i} \frac{Z_K}{\mathcal{R}_{Ki}} + \frac{1}{2}\sum_{i \neq j} \frac{1}{\mathcal{R}_{ij}} \tag{3}$$

where $\mathcal{R}_K$ and $\mathcal{R}_i$ are the positions of the N nuclei and the n electrons, respectively, in a space-fixed Cartesian coordinate system. The masses and charges of the K-th nucleus are denoted by m_K and Z_K.

The coordinates of the center of mass R_{CM} are defined by

$$M R_{CM} = \sum_{K=0}^{N-1} m_K \mathcal{R}_K + \sum_{i=1}^{n} \mathcal{R}_i \tag{4}$$

where M is the total mass of the system.

We further introduce the mass-weighted relative coordinates for the nuclei

$$R_k = \sqrt{\frac{\mu_k}{M}}(\mathcal{R}_K - \tilde{\mathcal{R}}_K) \; ; \; k = 1, N-1 \tag{5}$$

where each new coordinate is defined with respect to the center of mass $\tilde{\mathcal{R}}_K$ of the previously considered nuclei

$$\tilde{\mathcal{R}}_K \sum_{L=0}^{K-1} m_L = \sum_{L=0}^{K-1} m_L \mathcal{R}_L \tag{6}$$

and μ_K is the reduced mass of nucleus K and the total mass of the nuclei already introduced

$$\frac{1}{\mu_K} = \frac{1}{m_K} + \frac{1}{\sum\limits_{L=0}^{K-1} m_L} \tag{7}$$

The relative coordinates of the electrons are defined with respect to the center of mass of all nuclei

$$r_i = \mathcal{R}_i - \bar{\mathcal{R}}_K \tag{8}$$

In this coordinate system the Lagrangian is

$$L = \frac{1}{2} M R_{CM}^2 + \frac{1}{2} M \sum_{K=1}^{N-1} R_K^2 + \frac{1}{2} \sum_{i=1}^{n} r_i^2 - \frac{1}{2M} \left(\sum_{i=1}^{n} r_i \right)^2 - V(R, r) \tag{9}$$

where R and r represents collectively all nuclear and electronic coordinates respectively except R_{CM}. The center of mass motion is completely separated since it does not appear in the potential, and it will be neglected from now on. The fourth term in Eq. 9 is called the mass polarization term.

Introducing the conjugate momenta

$$P_K = \frac{\partial L}{\partial R_K} \tag{10}$$

$$P_i = \frac{\partial L}{\partial r_i} \tag{11}$$

We construct the classical Hamiltonian by

$$H = \sum_K P_K R_K + \sum_i P_i r_i - L \tag{12}$$

explicitly

$$H = \frac{1}{2M} \sum_{K=1}^{N-1} P_K^2 + \frac{1}{2} \sum_{i=1}^{n} P_i^2 + \frac{1}{2M_{\rm nuc}} \left(\sum_{i=1}^{n} P_i \right)^2 + V(R, r) \tag{13}$$

where $M_{\rm nuc}$ is the total mass of all nuclei

Replacing the momenta by their quantum mechanical operators one obtains the quantum mechanical Hamiltonian operator

$$H = T_{\rm nuc} + H_{el}(R) + H_{mp} \tag{14}$$

where

$$T_{\rm nuc} = -\frac{1}{2M} \sum_{K=1}^{N-1} \nabla_K^2 \tag{15}$$

is the nuclear Kinetic Energy operator,

$$H_{el}(R) = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 + V(R, r) \tag{16}$$

is the Electronic Hamiltonian operator which depends parametrically on the nuclear coordinates but it is independent of the nuclear masses, and

$$H_{mp} = -\frac{1}{2M_{\rm nuc}} \left(\sum_{i=1}^{n} \nabla_i \right)^2 \tag{17}$$

is the Mass Polarization operator.

For each nuclear geometry, the Electronic Hamiltonian possess a complete set of eigenfunctions. Hence, one can write the solution of Schroedinger equation

$$H\Psi = E\Psi \tag{18}$$

like an expansion over the orthonormal eigenfunctions of the Electronic Hamiltonian

$$H_{el}(R)\psi_{\mu}(R,r) = W_{\mu}(R)\psi_{\mu}(R,r) \tag{19}$$

as

$$\Psi(R,r) = \sum_{\mu} \chi_{\mu}(R)\psi_{\mu}(R,r) \tag{20}$$

where the expansion coefficients are independent of the electronic coordinates. Different basis of electronic eigenfunctions are used for each nuclear configuration R. One should be careful to ensure that the basis functions vary smoothly as one changes the nuclear configuration, in particular when degeneracies occur among the eigenfunctions.

In principle one may expand the total molecular wave function for an arbitrary nuclear configuration R in the complete set of electronic eigenfunctions at one particular nuclear configuration R^{o}

$$\Psi(R,r) = \sum_{\mu} \zeta(R)\psi_{\mu}(R^{o},r) \tag{21}$$

When the summations are infinite, both expansions (20 and 21) are exact. If the summations are truncated after one or few terms, the first expansion is more flexible over the complete PES, because of the extra freedom of having a different electronic wave function for each nuclear configuration.

To determine the expansion coefficients following Born, we insert the expansion Eq. (20) into the Schroedinger equation, Eq. (18), multiply on the left by $\psi^*_\mu(R,r)$ and integrate over the electronic coordinates. The resulting differential equations for the expansion coefficients are

$$\left[-\frac{1}{2M}\sum_{h=1}^{N-1}\nabla_h^2 + W(R) + \frac{1}{M}C_{\mu\mu}(R) - E\right]\chi_\mu(R) = -\frac{1}{M}\sum_{\nu\neq\mu} C_{\mu\nu}(R)\chi_\nu(R) \tag{22}$$

where

$$C_{\mu\nu}(R) = \sum_{h=1}^{N-1}\left[-\imath A^K_{\mu\nu}(R)\,\nabla_h + B^h_{\mu\nu}(R)\right] + D_{\mu\nu}(R) \tag{23}$$

The quantities entering in the above equation are the first order non adiabatic coupling matrix elements (NACME's)

$$A^K_{\mu\nu}(R) = \langle\psi_\mu(R,r)| - \imath\nabla_K|\psi_\nu(R,r)\rangle \tag{24}$$

the second-order NACME's

$$B^K_{\mu\nu}(R) = -\frac{1}{2}\langle\psi_\mu(R,r)|\nabla^2_h|\psi_\nu(R,r)\rangle \tag{25}$$

and the mass polarization

$$D^K_{\mu\nu}(R) = -\frac{M}{2M_{\text{nuc}}}\langle\psi_\mu(R,r)|\left[\sum_{i=1}^{n}\nabla_i\right]^2|\psi_\nu(R,r)\rangle \tag{26}$$

The above form of the Schroedinger equation is exact. No approximations have yet been introduced

The Schroedinger equation is greatly simplified if we neglect all matrix elements $C_{\mu\nu}(R)$ This results in the Born-Oppenheimer adiabatic wave function

$$\Psi^{BO}_{I\mu} = \chi_{I\mu}(R)\psi_\mu(R,r) \tag{27}$$

where the nuclear wave functions $\chi_{I\mu}(R)$ are the solutions of the equation

$$H^{BO}_\mu(R)\chi_{I\mu}(R) = E_{I\mu}\chi_{I\mu}(R) \tag{28}$$

$$H^{BO}_\mu(R) = -\frac{1}{2M}\sum_{h=1}^{h-1}\nabla^2_h + W_\mu(R) \tag{29}$$

For each electronic state there is a set of nuclear wave functions representing different nuclear states These are enumerated by the index I

In the Born-Oppenheimer approximation the electronic energy $W_\mu(R)$ acts as a potential for the nuclei This is equivalent to assuming that the electrons adjust instantaneously to the motion of the nuclei There is thus a different

Born-Oppenheimer Hamiltonian for each electronic state. The diagonal elements $C_{\mu\mu}(R)$ are sometimes retained in the Born-Oppenheimer Hamiltonian since they do not couple different electronic states, and this is referred to as the Adiabatic Approximation. Note that in the Adiabatic Approximation, the potential for the nuclei depends on the nuclear masses since the correction $C_{\mu\mu}(R)$ is mass dependent

Second Quantization

Second Quantization uses the occupation-number representation It is a very convenient representation to present most of Quantum Chemistry, and provides an unifying formulation for both semi empirical and ab-initio methods

In this section, we briefly introduce the essential ideas of second quantization as well as define our notation A more complete introduction to second quantized methods can be found elsewhere [57, 65, 68, 69]

In first quantization, the electronic Hamiltonian is written as

$$H_{el}(R) = \sum_{i=1}^{n} h(i) + \sum_{i<j} g(i,j) + \sum_{K<L} \frac{Z_K Z_L}{R_{KL}} \tag{30}$$

where the last term is just a constant for each nuclear configuration and can be added at the end of the calculation Hence we are interested in

$$H = \sum_{i=1}^{n} h(i) + \sum_{i<j} g(i,j) \tag{31}$$

where

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_{K=1}^{N} \frac{Z_K}{R_{Ki}} \tag{32}$$

is an one-electron operators and

$$g(i,j) = \sum_{i<j} \frac{1}{r_{ij}} \tag{33}$$

is the two-electron part of the Hamiltonian.

Electrons are fermions, so a wave function describing their motion must be antisymmetric under interchange of any two particles. This is a property of functions constructed as a linear combination of Slater determinants

$$\psi(x_1, x_2, \ldots, x_n) = \sum_{S} C_S \psi_S(x_1, x_2, \ldots, x_n) \tag{34}$$

where x_i is the coordinate (spacial and spin) of the i th electron and

$$\psi_S(x_1, x_2, \ldots, x_n) = (N!)^{-1/2} \det|\phi_t(x_1) \ldots \phi_s(x_{n-1})\phi_r(x_n)| \equiv |\phi_t \ldots \phi_s\phi_r| \tag{35}$$

The $\{\phi_i\}$ is an orthonormal (without loss of generality) one electron basis set. These one-electron function are called spin orbitals.

Slater determinantal wave functions involving orthonormal spin orbitals ϕ_i can be represented in terms of products of creation operators on the so-called vacuum ket $|vac\rangle$.

$$r^\dagger s^\dagger \ldots t^\dagger |vac\rangle \leftrightarrow |\phi_t \ldots \phi_s\phi_r| \tag{36}$$

The fundamentals of the second quantization are summarized in table 1.

Table 1 Fundamentals of second quantization

Basis vectors	$\vert\mathbf{n}\rangle = \vert n_1, n_2, \ldots, n_m\rangle$, $n_i = 0, 1$ for $i = 1, 2, \ldots, m$
Inner product	$\langle \mathbf{n} \vert \mathbf{k} \rangle = \prod_{i=1}^{m} \delta_{n_i k_i}$
Creation operators	$i^\dagger \vert n_1, \ldots, 0_i, \ldots, n_m\rangle = \Gamma(\mathbf{n}) \vert n_1, \ldots, 1_i, \ldots, n_m\rangle$ $\Gamma(\mathbf{n}) = (-1)^{\left(\sum_{j=1}^{i-1} n_j\right)}$ $i^\dagger \vert n_1, \ldots, 1_i, \ldots, n_m\rangle = 0$
Annihilation operators	$i \vert n_1, \ldots, 1_i, \ldots, n_m\rangle = \Gamma(\mathbf{n}) \vert n_1, \ldots, 0_i, \ldots, n_m\rangle$ $i \vert n_1, \ldots, 0_i, \ldots, n_m\rangle = 0$
Anticommutation relations	$[i^\dagger, j]_+ = i^\dagger j + j i^\dagger = \delta_{ij}$ $[i^\dagger, j^\dagger]_+ = i^\dagger j^\dagger + j^\dagger i^\dagger = 0$ $[i, j]_+ = ij + ji = 0$
Number operators	$i^\dagger i \vert\mathbf{n}\rangle = n_i \vert\mathbf{n}\rangle$ $\sum i^\dagger i \vert\mathbf{n}\rangle = \sum n_i \vert\mathbf{n}\rangle$
Vacuum state	$\langle vac \vert vac \rangle = 1$ $i \vert vac \rangle = 0$

The second-quantized version of any operator is obtained by simply demanding that the operator, when "sandwiched" or "bracketed" between bra and ket vectors of the form $\prod_r \langle vac \vert r = (\prod_r r^\dagger \vert vac\rangle)^\dagger$ and $\prod_r r^\dagger \vert vac\rangle$, yields exactly the same result as arises in using the first quantized operator between corresponding Slater determinant wave function The results are shown in Table 2.

Table 2 Characteristics for operators in first and second quantization

First Quantization	Second Quantization
one- electron operator $\sum_i f(r_i, \sigma_i) = \sum_i f(i)$	one- electron operator $\sum_{pq} \langle \phi_p \vert f \vert \phi_q \rangle p^\dagger q = \sum_{pq} f_{pq} p^\dagger q$
two- electron operator $\frac{1}{2} \sum_{i \neq j} g(r_i, \sigma_i, r_j, \sigma_j) = \frac{1}{2} \sum_{i \neq j} g(i, j)$	two- electron operator $\frac{1}{2} \sum_{p,q,r,s} \langle \phi_p \phi_q \vert g \vert \phi_r \phi_s \rangle p^\dagger q^\dagger s r =$ $\frac{1}{2} \sum_{p,q,r,s} g_{pqrs} p^\dagger q^\dagger s r$
operators are independent of spin orbitals basis	operators depend on spin orbitals basis
operators depend on the number of electrons	operators are independent of the number of electrons
exact operators	projected operators

So the second-quantized form of the Electronic Hamiltonian (except for the constant nuclear repulsion term) is

$$H = h_{pq} p^\dagger q + \frac{1}{4} \langle pq \vert\vert rs \rangle p^\dagger q^\dagger s r \tag{37}$$

where

$$h_{pq} = \int \phi_p^*(x_1)\left(-\frac{1}{2}\nabla_1^2 + \sum_{K=1}^{N}\frac{Z_A}{R_{1A}}\right)\phi_q(x_1)\, d\mathbf{x}_1 \tag{38}$$

is the one-electron part, and the two-electron part is

$$\langle pq||rs\rangle = \int \phi_p^*(x_1)\phi_q^*(x_2)\frac{1}{r_{12}}(1 - P_{12})\phi_r^*(x_1)\phi_s^*(x_2)\, d\mathbf{x}_1 d\mathbf{x}_2 \tag{39}$$

and the Permutation Operator P_{12} is defined by

$$P_{12}\phi_r(x_1)\phi_s(x_2) = \phi_s(x_1)\phi_r(x_2)\ ,\ P_{12}|rs\rangle = |sr\rangle \tag{40}$$

We use through out this thesis i, j, k, l, m, n to represent occupied orbitals in the reference state (holes), a, b, c, d, f, g to represent unoccupied orbitals (particles), and p, q, r, s, t, u, v to represent any orbital. Repeated indexes implies summation over them, e.g. equation 37

CHAPTER 2
METHODS OF APPROXIMATION

The simple pictures used by chemists and physicists are based in the independent-particle model. The most widely used independent-particle model is the Hartree-Fock method. It generates the "best" spin orbitals set.

The Hartree-Fock method is important not only because it is in itself a good approximation but also because it is the starting point of many more accurate methods.

Here we will briefly describe the Hartree Fock method and review some of the most successful past Hartree-Fock methods for including the correlated motions of electrons. I focus on the Configuration Interaction Method (matrix diagonalization), Perturbation Theory, and the Coupled-Cluster Ansatz.

Within the Coupled-Cluster review, special attention will be given to Spin-symmetry Adapted Coupled-cluster — Configuration Interaction (SAC-CI) [1–18], where we proposed some corrections to the original work of Nakatsuji and co-workers. We also introduce a diagrammatic way to obtain the SAC-CI ground state directly over molecular orbitals.

Hartree–Fock

The Hartree-Fock method [27–32, 65, 68–71] consists in obtaining the set of spin-orbitals for which the energy is an extreme, when the wavefunction is approximated by a single Slater determinant constructed with those spin-orbitals, subject to the orthonormality condition

One writes a trial wavefunction as

$$\tilde{\psi} = |\phi_1\phi_2 \cdots \phi_N| \; ; \; \langle\phi_i|\phi_j\rangle = \delta_{ij} \tag{41}$$

which assures that $\langle\tilde{\psi}|\tilde{\psi}\rangle = 1$. By applying the Eckart's Variational Principle (VP) [72–78] with the restriction that the spin-orbitals continue to be an orthonormal set, i.e. $\langle\phi_i|\phi_j\rangle = \langle i|j\rangle = \delta_{ij}$, one obtains the Hartree-Fock equations. This is done by constructing a Lagrangian and introducing Lagrange's multipliers $\{\varepsilon_{kl}\}$ explicitly

$$\mathcal{L}[\tilde{\psi}] = H[\tilde{\psi}] - \sum_{kl} \varepsilon_{kl}\langle k|l\rangle \tag{42}$$

where

$$H[\tilde{\psi}] = \langle\tilde{\psi}|H|\tilde{\psi}\rangle = h_{kk} + \frac{1}{2}\langle kl||kl\rangle \tag{43}$$

hence

$$\delta\mathcal{L} = \delta H \tag{44}$$

If one constrains δH to be real, then $\varepsilon^*_{qp} = \varepsilon_{pq}$. So varying the orbitals and setting $\delta\mathcal{L} = \delta H = 0$, one gets

$$0 = \langle\delta p|\left\{\left[h + \left(\int d\mathbf{x}_2\, \phi^*_q(x_2)\frac{1}{\mathbf{r}_{12}}(1 - P_{12})\phi_q(x_2)\right)\right]|p\rangle - \varepsilon_{pq}|q\rangle\right\} + \begin{matrix}\textit{complex}\\ \textit{conjugate}\end{matrix} \tag{45}$$

Since the variations $\langle\delta k|$ are unrestricted then

$$f(x_1)\phi_p(x_1) = \varepsilon_{pq}\,\phi_q(x_1) \tag{46}$$

where $f(x)$ is called the Fock operator and is defined as

$$f(x_1)\phi_p(x_1) = \left[h(x_1) + \left(\int d\mathbf{x_2}\,\phi_q^*(x_2)\frac{1}{r_{12}}(1-P_{12})\phi_q(x_2)\right)\right]\phi_p(x_1) \tag{47}$$

For the closed-shell restricted Hartree-Fock (RHF) case or for the unrestricted Hartree-Fock (UHF) case $\bar{\varepsilon}$ is an hermitian matrix it can be diagonalized by a unitary transformation ($\varepsilon = \mathbf{U}\bar{\varepsilon}\mathbf{U}^\dagger$, $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}$), resulting in the canonical Hartree-Fock equations

$$f(x_1)\phi_k(x_1) = \varepsilon_l\,\phi_l(x_1)\delta_{kl} \tag{48}$$

A similar equation can also be derived for the general open-shell restricted Hartree-Fock case, but this derivation is more complex as is the form of $f(x_1)$

For systems with an even number of electrons (N), the RHF assumes

$$|0\rangle = \psi_{HF} = |\phi_1^\alpha\phi_1^\beta\phi_2^\alpha\phi_2^\beta \cdots \phi_{N/2}^\alpha\phi_{N/2}^\beta| \tag{49}$$

and the energy is then given by

$$E_{HF} = \langle 0|H|0\rangle = \varepsilon_{kk} - \frac{1}{2}\langle kl||kl\rangle + \frac{Z_K Z_L}{R_{KL}} \tag{50}$$

with

$$\varepsilon_{kk} = h_{kk} + \langle kl||kl\rangle \tag{51}$$

The exact solution of the RHF equations, i.e. α and β spin-orbitals have the same spacial part (orbital), result in the Hartree-Fock limit energy. The difference between the RHF limit value and the exact value of the nonrelativistic Electronic Hamiltonian is called correlation energy [42]. So by definition Restricted Hartree-Fock energy has no correlation, although physically it correlates the motion of electrons with different spins.

The solutions of the Hartree-Fock equations are usually attained by an expansion of the molecular orbitals $\{\phi_i\}$ over atomic orbitals $\{\varphi_k\}$, explicitly

$$\phi = \chi\mathbf{C}\ ,\ \phi_p = \chi_q C_{qp} \tag{52}$$

With this approximation the Fock equation for the closed shell case is written as

$$\mathbf{FC} = \epsilon\mathbf{SC} \tag{53}$$

where

$$F_{pq} = \langle\chi_p|f|\chi_q\rangle = \langle\chi_p|h|\chi_q\rangle + \sum_{rsv} C^*_{sv}C_{rv}\langle\chi_p\chi_s||\chi_q\chi_r\rangle \tag{54}$$

and

$$S_{pq} = \langle\chi_p|\chi_q\rangle \tag{55}$$

If all the integrals of equation 54 are evaluated from first principles, it is an ab-initio method [79]. Approximations are made to increase the speed and accuracy of the method and such approximations to the one-electron part, $D_{rs} = \sum_{v} C^{*}_{sv} C_{rv}$ and the two-electron integrals results in a series of semi-empirical methods [80-83].

Configuration Interaction

For most situations the HF method is able to give qualitative agreement with experiment. Examples are geometric structure, vibrational spectroscopy and the energy differences connected with conformational changes such as inversion and rotational barriers. Proton affinities and hydration energies are also well described by the Hartree Fock method. Common to all cases for which the HF method is applicable is that no drastic rearrangement takes place, while the system changes from state A to state B. No electron pairs are broken or formed, and the molecular orbitals are only slightly modified. The error connected with the HF approximation remains almost constant, and a qualitative agreement can be achieved. Many interesting problems, however, do not belong to this category, e.g. ionization energies, electronic excitation energies and especially important chemical reactions involving the formation of covalent bonds.

Methods more accurate are then necessary Historically, Configuration Interaction (CI)[41, 43, 45, 65, 68–71] was one of the first correlated method based in the molecular orbital theory, and, in fact, was originally the title given to all post Hartree-Fock methods Today, CI usually refers to methods of the variational type that results in *matrix* diagonalization

Expanding the wavefunction as

$$|\psi\rangle = (C_0 + C_i^a a^\dagger i + C_{ij}^{ab} a^\dagger b^\dagger j i + \dots)|0\rangle \tag{56}$$

where $\{C_i\}$ are variational parameters and applying the variational principle to

$$E[\psi] = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{57}$$

yields the secular equation

$$\mathbf{HC} = E\mathbf{C} \tag{58}$$

where ψ is the row vectors of configurations and $\mathbf{C}$ is the column vector of variational parameters The CI wavefunction can be written as

$$\mathbf{\Psi} = \psi\mathbf{C} \tag{59}$$

while $\mathbf{H}$ is the Hamiltonian matrix between the different configurations

$$H_{ij} = \langle\psi_i|H|\psi_j\rangle \tag{60}$$

The CI wavefunction is size extensive, only when all configurations within a basis set are included, which is called Full CI (CIF). The eigenvalues of the secular equation are upper bounds of the electronic states order by order [43, 44–48].

Size extensivity refers to the property that N non-interacting subsystems

$$H_A|\psi_A\rangle = E_A|\psi_A\rangle$$

$$\vdots \tag{61}$$

$$H_N|\psi_N\rangle = E_N|\psi_N\rangle$$

should have total energy given by the sum of its parts, i.e.

$$(H_A + H_B + \cdots + H_N)|\psi\rangle = (E_A + E_B + \cdots + E_N)|\psi\rangle \tag{62}$$

Perturbation Theory

Perturbation Theory (PT) [38–40, 47, 65, 68, 69, 84–89] assumes that the initial guess for the wavefunction is indeed a good one and expands the energy in terms of correction to this initial guess.

Rewriting the Scroedinger equation as

$$(\epsilon - H_o)|\psi\rangle = (V - E + \epsilon)|\psi\rangle \tag{63}$$

where ϵ is a shift parameter and assuming intermediate normalization, i.e

$$|\psi\rangle = |0\rangle + Q|\psi\rangle \tag{64}$$

where $Q|0\rangle = 0$, and $\langle 0|\psi\rangle = \langle 0|0\rangle = 1$, one obtains:

$$Q|\psi\rangle = (\varepsilon - H_o)^{-1} Q (V - E + \varepsilon)|\psi\rangle \tag{65}$$

and

$$\Delta E = E - E_o = \langle 0|V|\psi\rangle \tag{66}$$

where

$$E_o = \langle 0|H|0\rangle \tag{67}$$

and

$$Q = 1 - P = 1 - |0\rangle\langle 0| \tag{68}$$

$(\varepsilon - H_o)^{-1} Q = R$ is defined as the Resolvent , yielding

$$Q|\psi\rangle = R\, Q\, (V - E + \varepsilon)|\psi\rangle \tag{69}$$

For Rayleigh Schroedinger Perturbation Theory (RS) $\varepsilon = E_o$, thus

$$R_{RS} = (E_o - H_o)^{-1}\, Q \tag{70}$$

For Brillouin Wigner Perturbation Theory (BW) $\varepsilon = E$ thus

$$R_{BW} = R_{BW}(E) = (E - H_o)^{-1}\, Q \tag{71}$$

Iterating over the wavefunction equation 69 yields

$$|\psi\rangle = |0\rangle + R\,Q\,(V - E + \varepsilon)|0\rangle + \dots \tag{72}$$

$$= \sum_{n=0}^{\infty} [R\,Q\,(V - E + \varepsilon)]^n |0\rangle \tag{73}$$

$$= \sum_{n=0}^{\infty} |\psi^{(n)}\rangle \tag{74}$$

and

$$\Delta \mathrm{E} = \langle 0|V|\psi\rangle \tag{75}$$

$$= \sum_{n=0}^{\infty} \langle 0|V\,[R\,Q\,(V - E + \varepsilon)]^n|0\rangle \tag{76}$$

$$= \sum_{n=1}^{\infty} E^n \tag{77}$$

Since the HF wavefunction in many cases provides a reasonable description of the electronic structure, it is natural to improve on it by perturbation theory. In Møller-Plesset and Many-Body Perturbation Theory (MBPT), the partitioning of the Hamiltonian takes this in consideration, explicitly

$$H_0^{MP} = f_{pq} p^{\dagger} q \tag{78}$$

$$V^{MP} = \frac{1}{4}\langle pq||rs\rangle p^{\dagger}q^{\dagger}sr - \langle pk||qk\rangle p^{\dagger}q \tag{79}$$

$$E^{1}_{MP} = -\frac{1}{2}\langle kl||kl\rangle \tag{80}$$

and

$$E_{HF} = E^{0}_{MP} + E^{1}_{MP} \tag{81}$$

Rayleigh-Schroedinger perturbation theory can be shown to be size extensive order by order [68] but it is not an upper bound. Brillouin Wigner Perturbation Theory is not size-extensive but its odd-orders are upper bound for the energy. For example equation 81 implies that Hartree-Fock is size extensive.

The main disadvantage of perturbation theory is the assumption of a Hamiltonian partitioning, $H_0 + V$, that is rapidly convergent. To insure this may require a reference function of several configurations and such theories at higher orders become quite complex.

Coupled Cluster Theory

The basic idea of Coupled Cluster theory [52, 53, 65, 68, 69, 89, 90] is to treat the interaction among the electrons as an interaction among electrons within clusters and a coupling between these clusters. The coupling between the clusters of electrons is obtained by writing the wavefunction as an exponential of the cluster operator T acting on a single determinant reference wave function. The reference wave function is most often assumed to be a Hartree-Fock state

$$|CC\rangle = \exp(T)|0\rangle \tag{82}$$

where the cluster operator T consists of one electron, two-electron, ..., N-electron clusters

$$T = T_1 + T_2 + \cdots + T_\Lambda \tag{83}$$

with

$$T_1 = t_i^a a^\dagger i \tag{84}$$

$$T_2 = \frac{1}{4} t_{ij}^{ab} a^\dagger i b^\dagger j \tag{85}$$

Again the labels i, j, k, l and a, b, c, d are used for occupied (hole) and virtual (particle) spin-orbitals in the reference determinant, respectively. The cluster operator truncates at excitation level Λ, the number of electrons in the system. In a shorthand notation the cluster operator can be written as

$$T = \sum_{\mu=1}^{\Lambda} T_\mu = \sum_{\mu=1}^{\Lambda} t_\mu \tau_\mu = \mathbf{t}\tau \tag{86}$$

where t_μ denotes the cluster amplitudes at excitation level μ and τ_μ is the corresponding excitation operator. The excitation operators satisfy

$$\tau_\mu^\dagger|0\rangle = 0 \tag{87}$$

$$\langle 0|\tau_{\mu}^{\dagger}\tau_{\nu}|0\rangle = \delta_{\mu\nu} \tag{88}$$

$$[\tau_{\mu}, \tau_{\nu}] = 0 \ \Rightarrow \ [T_{\mu}, T_{\nu}] = 0 \tag{89}$$

Hence the Schroedinger equation takes the form

$$H\exp(T)|0\rangle = E\exp(T)|0\rangle \tag{90}$$

or rewriting in a more convenient form

$$\exp(-T)H\exp(T)|0\rangle = E|0\rangle \tag{91}$$

which defines an effective Hamiltonian

$$\begin{aligned} H_{eff} = \exp(-T)H\exp(T) = H + [H,T] + \frac{1}{2!}[[H,T],T] + \\ \frac{1}{3!}[[[H,T],T],T] + \frac{1}{4!}[[[[H,T],T],T],T] \end{aligned} \tag{92}$$

The truncation after four commutators is exact regardless of the excitation level at which T is truncate. The truncation is due to the fact that the Hamiltonian contains at most a two-electron operator

The Coupled Cluster equation is solved, in general by requiring that Eq. 91 holds in the K fold excitation manifold, where K is the excitation level. Explicitly

$$E = \langle 0|\exp(-T)H\exp(T)|0\rangle = \langle 0|H\exp(T)|0\rangle \tag{93}$$

and

$$\langle\mu|\exp(-T)H\exp(T)|0\rangle = 0 \tag{94}$$

where

$$\langle\mu| = \langle 0|\tau_{\mu}^{\dagger} \tag{95}$$

The energy in the Coupled Cluster model is not variational in the sense that it is not an expectation value of the Hamiltonian. The minimization of the quantity

$$E = \frac{\langle 0|\exp(T)^{\dagger}H\exp(T)|0\rangle}{\langle 0|\exp(T)^{\dagger}\exp(T)|0\rangle} \tag{96}$$

would give rise to a variational energy with the CC ansatz of the wavefunction. But this series does not truncate.

The CC equations are non-linear, hence they have more than one solution. There is at least one solution which is size-extensive, which is the solution obtained by the usual techniques. This solution can be viewed as an infinite summation of MBPT series [68].

The advantage of the truncated CC approach over the truncated CI method is that the former is size-extensive and give a very compact parametrization. However there is not a complete satisfactory formulation of the CC approach capable of treating excited states or near-degeneracy situations [68]. The advantage of the truncated CI method is that it always supplies a well behaved upper bound to the energy.

Spin Symmetry Adapted Coupled Cluster

One of the more promising CC based methods for excited states is the Spin-symmetry Adapted Coupled-cluster – Configuration Interaction (SAC-CI) approach [1–18] We will concentrate in the singlet case here, and present a diagrammatic representation of the SAC-CI method.

The SAC-CI method is used to calculate transition energies which takes advantage of the spin symmetry to reduce the number of integrals

The SAC-CI method was introduced by H Nakatsuji [1–18] It has a Coupled Cluster wavefunction for the ground state. The multielectron basis set is generated from single excitations The excited states are obtained in a fashion paralleling the CI method [7].

The ground state wavefunction is written as

$$|\psi_g\rangle = \hat{O}_s \exp(\hat{S})|0\rangle = \hat{O}_s|\psi'_g\rangle \tag{97}$$

where $\hat{S} = S_1 + S_2 + \quad + S_N$ is the spin-symmetry adapted cluster operator with $S_1 = C_i^a S_i^{a\dagger}$ $S_2 = C_{ij}^{ab} S_{ij}^{ab\dagger}$, etc, O_s is the spin-projector of the ground state and $|0\rangle$ is the reference single determinant.

$S_i^{a\dagger}$ is $S_i^{a\dagger} = \frac{1}{\sqrt{2}}(a_\alpha^\dagger i_\alpha + a_\beta^\dagger i_\beta)$ for singlet excitations, $S_i^{a\dagger} = a_\alpha^\dagger i_\beta$ for triplet excitations etc

One solves

$$(\hat{H} - E)\hat{O}_s \exp(\hat{S})|0\rangle = 0 \tag{98}$$

to obtain the spin adapted CC amplitudes $\{C\}$ by projecting the above expression on a set of lower order excitations out of the reference function, as in equations 93 and 94

The multielectron basis set $\{\phi_k\}$ for the excited (or ionic) states is generated by

$$|\phi_k\rangle = \Lambda_k \hat{Q}\hat{O}_r R_k^\dagger|\psi_g'\rangle \qquad (99)$$

where Λ_k is a normalizing constant, $\hat{Q}$ $(\hat{Q} = 1 - |\psi_g\rangle\langle\psi_g|)$ projects into the orthogonal space to $|\psi_g\rangle$, $\hat{O}_r$ is the projector into the desired spin symmetry and $R_k^\dagger$ is the symmetry adapted excitation (or ionization or electron attachment) operator

Thus one can write a wavefunction for an excited state as

$$|\psi_e\rangle = |\phi_k\rangle d_k + |\psi_g\rangle d_o \qquad (100)$$

$d_o = 0$ if the excited state and the ground state do not have the same spin symmetry or the ground state was obtained variationally

In any case, one has to diagonalize

$$\mathbf{H}\mathbf{d} = \mathbf{d}E \qquad (101)$$

where $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$, and $\mathbf{d} = (d_1, d_2, \ldots, d_m)$, to obtain the excited state energies and wave functions Such a procedure re-introduces unlinked clusters and the method looses its size-extensivity, although this appears to be of minor importance in numerical examples. However, diagonalization appears to be a necessary step to obtain non-interacting spectroscopic states.

For a singlet ground state and singlet excited states, Nakatsuji [1–4] assumes the following

$$|\psi_g\rangle = \exp(\hat{S})|0\rangle \approx \{1 + \hat{S} + \frac{1}{2!}\hat{S}^2\}|0\rangle \qquad (102)$$

where $\hat{S} \approx S_1 + S_2$

$S_1 = C_i^a S_i^{a\dagger}$ and $S_2 = C_{ij}^{ab} S_i^{a\dagger} S_j^{b\dagger}$ and

$$S_i^{a\dagger} = \frac{1}{\sqrt{2}}(a_{\alpha}^{\dagger} i_{\alpha} + a_{\beta}^{\dagger} i_{\beta}) \qquad (103)$$

Thus,

$$|\psi_g\rangle = \{1 + C_i^a S_i^{a\dagger} + (C_{ij}^{ab} + \frac{1}{2}C_i^a C_j^b)S_i^{a\dagger} S_j^{b\dagger} + C_i^a C_{jk}^{bc} S_i^{a\dagger} S_j^{b\dagger} S_k^{c\dagger} + \frac{1}{2}C_{ij}^{ab} C_{kl}^{cd} S_i^{a\dagger} S_j^{b\dagger} S_k^{c\dagger} S_l^{d\dagger}\}|0\rangle \qquad (104)$$

To obtain the cluster amplitudes, he further requires that

$$\begin{aligned} \langle 0|H - E|\psi_g\rangle &= 0 \\ \langle S_i^{a\dagger} 0|H - E|\psi_g\rangle &= 0 \\ \langle S_i^{a\dagger} S_j^{b\dagger} 0|H - E|\psi_g\rangle &= 0 \end{aligned} \qquad (105)$$

which means requiring that $(H - E)|\psi_g\rangle = 0$ in the sub-space spanned by the reference function, single and double excitations with respect to this function

The amplitudes can also be obtained variationally, by applying the variational principle to

$$W(\{C\}) = \frac{\langle\psi_g|\hat{H} - E|\psi_g\rangle}{\langle\psi_g|\psi_g\rangle} \tag{106}$$

The singlet excited states basis set is generated by

$$|\phi_i^a\rangle = \Lambda_{1a} Q S_i^{a\dagger}|\psi_g\rangle \tag{107}$$

Hence, $|\psi_e\rangle = |\phi_i^a\rangle d_i^a + |\psi_g\rangle d_0$. The solutions are obtained by diagonalizing $\mathbf{H}\mathbf{d} = \mathbf{d}E$. If $|\psi_g\rangle$ is obtained variationally, then d_0 is considered zero because it will not couple with the other functions through the Hamiltonian.

The Nakatsuji ansatz for singlet ground state $|\psi_g\rangle = \exp(S)|0\rangle \approx (1 + S + \frac{1}{2!}S^2)|0\rangle$ leads to disconnected terms in the reference energy expression, since the exponential operator is truncated at this order.

I suggest that

$$|\psi_g\rangle = \exp(S)|0\rangle \approx (1 + \hat{S} + \frac{1}{2!}S^2 + \frac{1}{3!}\hat{S}^3 + \frac{1}{4!}S^4)|0\rangle \tag{108}$$

is better, because then

$$\begin{aligned}|\psi_g\rangle = \{1 + C_i^a S_i^{a\dagger} + (C_{ij}^{ab} + \tfrac{1}{2}C_i^a C_j^b)S_i^{a\dagger}S_j^{b\dagger} +\\ +(C_i^a C_{jk}^{bc} + \tfrac{1}{6}C_i^a C_j^b C_k^c)S_i^{a\dagger}S_j^{b\dagger}S_k^{c\dagger} +\\ \frac{1}{2}(C_{ij}^{ab}C_{kl}^{cd} + C_i^a C_j^b C_{kl}^{cd} + \frac{1}{12}C_i^a C_j^b C_k^c C_l^d)S_i^{a\dagger}S_j^{b\dagger}S_k^{c\dagger}S_l^{d\dagger}\}|0\rangle\end{aligned} \tag{109}$$

if we assume $S \approx S_1 + \hat{S}_2$. This new expression for the ground state leads to connected terms only, in the coupled equations. That is, all the unlinked terms cancel in lower order.

$$\langle 0|H - E|\psi_g\rangle = 0 \tag{110}$$

$$\langle S_1^{a\dagger} 0|H - E|\psi_g\rangle = 0 \tag{111}$$

$$\langle S_1^{a\dagger} S_2^{ab\dagger} 0|\hat{H} - E|\psi_g\rangle = 0 \tag{112}$$

and the resultant energy is size-extensive at least until matrix diagonalization

In terms of the molecular orbitals we have

$$f_{pq} = h_{pq} + \langle\langle pi|qi\rangle\rangle \tag{113}$$

$$\langle\langle pq|rs\rangle\rangle = 2\langle pq||rs\rangle - \langle pq||sr\rangle \tag{114}$$

$$E^0 = E_{HF} = \langle 0|H|0\rangle = 2f_{ii} - \langle\langle ij|ij\rangle\rangle \tag{115}$$

$$\langle pr|qs\rangle = \langle pq|rs\rangle = \int dr_1 dr_2 \phi_p^*(r_1)\phi_q^*(r_2)\frac{1}{r_{12}}\phi_r(r_1)\phi_s(r_2) \tag{116}$$

Assuming Eq. 109 and using Eqs. 110,111,112, one obtains a set of coupled equations in terms of molecular orbitals instead of spin-orbitals

1. $\langle 0|\hat{\mathbf{H}} - \mathbf{E}|\psi_g\rangle = 0$

$$\begin{aligned} E &= E^{\pi} + \sqrt{2}C^{a}_{i} f_{ia} + (C^{ab}_{ij} + \tfrac{1}{2}C^{a}_{i}C^{b}_{j})((ij|ab)) \\ E &= 2f_{ii} - ((ij|ij)) + \sqrt{2}C^{a}_{i} f_{ia} + (C^{ab}_{ij} + \tfrac{1}{2}C^{a}_{i}C^{b}_{j})((ij|ab)) \end{aligned} \tag{117}$$

2. $\langle 0|\mathbf{S}^{f}_{m}(\hat{\mathbf{H}} - \mathbf{E})|\psi_g\rangle = 0$

$$\begin{aligned} &\sqrt{2}f_{mf} + C^{a}_{m} f_{fa} - C^{f}_{i} f_{im} + C^{a}_{i}((if|am)) + \\ &+\sqrt{2}\left(2C^{af}_{im} - C^{af}_{mi} - \tfrac{1}{2}C^{f}_{i}C^{a}_{m}\right) f_{ia} + \\ &+\sqrt{2}\left(C^{ab}_{im} + \tfrac{1}{2}C^{a}_{i}C^{b}_{m}\right)((if|ab)) + \\ &-\sqrt{2}\left(C^{af}_{ij} + \tfrac{1}{2}C^{a}_{i}C^{f}_{j}\right)((ij|am)) + \\ &+\left(2C^{a}_{i}C^{bf}_{jm} - C^{f}_{i}C^{ab}_{mj} - C^{a}_{m}C^{fb}_{ij} - C^{a}_{i}C^{bf}_{mj} - \tfrac{1}{2}C^{a}_{i}C^{f}_{j}C^{b}_{m}\right)((ij|ab)) + \\ &+C^{f}_{m}\langle 0|\hat{H} - E|\psi_g\rangle = 0 \end{aligned} \tag{118}$$

3 $\langle 0|\mathbf{S}^{f}_{m}\mathbf{S}^{g}_{n}(\hat{\mathbf{H}} - \mathbf{E})|\psi_g\rangle = 0$

$$\begin{aligned} &((fg|mn)) + \\ &+\frac{1}{\sqrt{2}}\{C^{a}_{m}((fg|an)) + C^{a}_{n}((fg|ma))\} + \\ &-\frac{1}{\sqrt{2}}\{C^{f}_{i}((ig|mn)) + C^{g}_{i}((if|nm))\} + \end{aligned} \tag{119}$$

$$+\{-2C^{fg}_{mi}+C^{gf}_{mi}\}f_{in}+\{-2C^{fg}_{in}+C^{gf}_{in}\}f_{im}+$$
$$-\{-2C^{fa}_{mn}+C^{af}_{mn}\}f_{ga}-\{-2C^{ag}_{mn}+C^{ga}_{mn}\}f_{fa}+$$

$$+\{2C^{fa}_{mi}-C^{af}_{mi}-\frac{1}{2}C^{a}_{m}C^{f}_{i}\}((ig|an))+$$
$$+\{2C^{ga}_{ni}-C^{ag}_{ni}-\frac{1}{2}C^{a}_{n}C^{g}_{i}\}((if|am))+$$
$$-C^{ga}_{mi}((if|an))-\{C^{ag}_{mi}+\frac{1}{2}C^{a}_{m}C^{g}_{i}\}((if|na))+$$
$$-C^{fa}_{ni}((ig|am))-\{C^{af}_{ni}+\frac{1}{2}C^{a}_{n}C^{f}_{i}\}((ig|ma))+$$

$$+\{C^{ab}_{mn}+\frac{1}{2}C^{a}_{m}C^{b}_{n}\}((fg|ab))+$$
$$+\{C^{fg}_{ij}+\frac{1}{2}C^{f}_{i}C^{g}_{j}\}((ij|mn))+$$
$$+\frac{1}{\sqrt{2}}\{-2C^{a}_{m}C^{gf}_{ni}+C^{a}_{m}C^{fg}_{ni}\}f_{ia}+$$
$$+\frac{1}{\sqrt{2}}\{-2C^{a}_{n}C^{fg}_{mi}+C^{a}_{n}C^{gf}_{mi}\}f_{ia}+$$
$$+\frac{1}{\sqrt{2}}\{-2C^{g}_{i}C^{fa}_{mn}+C^{f}_{i}C^{ga}_{mn}\}f_{ia}+$$
$$+\frac{1}{\sqrt{2}}\{-2C^{f}_{i}C^{ag}_{mn}+C^{g}_{i}C^{af}_{mn}\}f_{ia}+$$

$$+\frac{1}{\sqrt{2}}\{-2C^{f}_{j}C^{ga}_{ni}+C^{g}_{j}C^{fa}_{ni}\}((ij|am))+$$

$$
\begin{aligned}
&+\frac{1}{\sqrt{2}}\{-2C^{a}_{i}C^{fg}_{jn}+C^{a}_{i}C^{gf}_{jn}\}((ij|am))+\\
&+\frac{1}{\sqrt{2}}\{C^{f}_{j}C^{ag}_{ni}+C^{g}_{i}C^{fa}_{jn}+C^{a}_{n}C^{gf}_{ij}\}((ij|am))+
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{\sqrt{2}}\{-2C^{g}_{j}C^{fa}_{mi}+C^{f}_{j}C^{ga}_{mi}\}((ij|an))+\\
&+\frac{1}{\sqrt{2}}\{-2C^{a}_{i}C^{gf}_{jm}+C^{a}_{i}C^{fg}_{jm}\}((ij|an))+\\
&+\frac{1}{\sqrt{2}}\{C^{g}_{j}C^{af}_{mi}+C^{f}_{i}C^{ga}_{jm}+C^{a}_{m}C^{fg}_{ij}\}((ij|an))+
\end{aligned}
\tag{124}
$$

$$
\begin{aligned}
&-\frac{1}{\sqrt{2}}\{-2C^{b}_{m}C^{ag}_{in}+C^{b}_{n}C^{ag}_{im}\}((if|ab))+\\
&-\frac{1}{\sqrt{2}}\{-2C^{a}_{i}C^{bg}_{mn}+C^{a}_{i}C^{bg}_{nm}\}((if|ab))+\\
&-\frac{1}{\sqrt{2}}\{C^{g}_{i}C^{ba}_{mn}+C^{b}_{m}C^{ag}_{ni}+C^{a}_{n}C^{bg}_{mi}\}((if|ab))+
\end{aligned}
\tag{125}
$$

$$
\begin{aligned}
&-\frac{1}{\sqrt{2}}\{-2C^{b}_{n}C^{af}_{im}+C^{b}_{m}C^{af}_{in}\}((ig|ab))+\\
&-\frac{1}{\sqrt{2}}\{-2C^{a}_{i}C^{fb}_{mn}+C^{a}_{i}C^{bf}_{mn}\}((ig|ab))+\\
&-\frac{1}{\sqrt{2}}\{C^{f}_{i}C^{ab}_{mn}+C^{a}_{m}C^{bf}_{ni}+C^{b}_{n}C^{af}_{mi}\}((ig|ab))+
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{2\sqrt{2}}\{C^{a}_{n}C^{g}_{i}C^{f}_{j}((ij|am))+C^{a}_{m}C^{f}_{i}C^{g}_{j}((ij|an))\}+\\
&-\frac{1}{2\sqrt{2}}\{C^{g}_{i}C^{b}_{m}C^{a}_{n}((if|ab))+C^{f}_{i}C^{a}_{m}C^{b}_{n}((ig|ab))\}+
\end{aligned}
$$

$$+\{-2C^{bg}_{mn}C^{af}_{ij}+C^{bf}_{mn}C^{ag}_{ij}\}((ij|ab))+$$
$$+\{-2C^{fa}_{mn}C^{gb}_{ij}+C^{ga}_{mn}C^{fb}_{ij}\}((ij|ab))+$$
$$-\{-2C^{fa}_{mi}C^{gb}_{nj}+C^{ga}_{mi}C^{fb}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{2C^{ab}_{mn}C^{fg}_{ij}+C^{af}_{mi}C^{bg}_{nj}+C^{bg}_{mi}C^{af}_{nj}\}((ij|ab))+$$

$$+\frac{1}{2}\{-2C^{fg}_{mi}C^{ab}_{nj}+C^{gf}_{mi}C^{ab}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{fa}_{mi}C^{bg}_{nj}+C^{ga}_{mi}C^{bf}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{af}_{mi}C^{gb}_{nj}+C^{ag}_{mi}C^{fb}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{ba}_{mi}C^{gf}_{nj}+C^{ba}_{mi}C^{fg}_{nj}\}((ij|ab))+$$

$$+\frac{1}{2}\{-2C^{a}_{i}C^{g}_{j}C^{fb}_{mn}+C^{a}_{i}C^{f}_{j}C^{gb}_{mn}+C^{a}_{m}C^{b}_{n}C^{fg}_{ij}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{a}_{i}C^{f}_{j}C^{bg}_{mn}+C^{a}_{i}C^{g}_{j}C^{bf}_{mn}+C^{f}_{i}C^{g}_{j}C^{ab}_{mn}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{a}_{m}C^{f}_{i}C^{gb}_{nj}+C^{a}_{m}C^{g}_{i}C^{fb}_{nj}+C^{a}_{m}C^{f}_{i}C^{bg}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{b}_{m}C^{a}_{i}C^{gf}_{nj}+C^{b}_{m}C^{a}_{i}C^{fg}_{nj}+C^{b}_{m}C^{g}_{i}C^{af}_{nj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{a}_{n}C^{g}_{i}C^{fb}_{mj}+C^{a}_{n}C^{f}_{i}C^{gb}_{mj}+C^{a}_{n}C^{g}_{i}C^{bf}_{mj}\}((ij|ab))+$$
$$+\frac{1}{2}\{-2C^{b}_{n}C^{a}_{i}C^{fg}_{mj}+C^{b}_{n}C^{a}_{i}C^{gf}_{mj}+C^{b}_{n}C^{f}_{i}C^{ag}_{mj}\}((ij|ab))+$$

$$+\frac{1}{4}C^{f}_{i}C^{g}_{j}C^{a}_{m}C^{b}_{n}((ij|ab))+$$

$$\begin{aligned}
&+2\{C^{fg}_{mn}+\frac{1}{2}C^{f}_{m}C^{g}_{n}\}\langle 0|\hat{H}-E|\psi_{g}\rangle+\\
&-\{C^{gf}_{mn}+\frac{1}{2}C^{g}_{m}C^{f}_{n}\}\langle 0|\hat{H}-E|\psi_{g}\rangle+\\
&+C^{f}_{m}\langle 0|S^{g}_{n}(H-E)|\psi_{g}\rangle+\\
&+C^{g}_{n}\langle 0|S^{f}_{m}(\hat{H}-E)|\psi_{g}\rangle+\\
&-\frac{1}{2}C^{f}_{n}\langle 0|S^{g}_{m}(H-E)|\psi_{g}\rangle+\\
&-\frac{1}{2}C^{g}_{m}\langle 0|S^{f}_{n}(\hat{H}-E)|\psi_{g}\rangle
\end{aligned}$$

Diagrammatic Rule for a SAC-CI Singlet Ground State

The expressions in Eqs 117,118,119 can be derived using diagrammatic rules that we introduce here The rules are different from the usual ones in PT, because we are using molecular orbitals instead of spin-orbitals, and have spin eigenstates restrictions

Diagrammatic Rules

1 Full arrows indicates sum over index

2. Sign. $(-1)^{h+p+l_o+p_o}$ where

h is the number of holes summed over

p is the number of open lines divided by 2 (or the number of pairs of open lines)

l_α is the number of independent α loops

p_α is the number of independent α paths

3 $(\frac{1}{\sqrt{2}})^{\#\text{ of equivalent lines}}$, and open lines are never equivalent

4 $(2)^{l_\alpha + p_\alpha}$ all continuous paths or loops can be α or β, except those where the particle and respective hole are not in same path (or loop)

5 $(\frac{1}{\sqrt{2}})^p$ each pair of open lines contribute with this because $S_n^{f\dagger} = \frac{1}{\sqrt{2}}(f_\alpha^\dagger m_\alpha + f_\beta^\dagger m_\beta)$

6 contributes with $\langle in|\hat{F}|out\rangle^* = \langle out|\hat{F}|in\rangle$

7 contributes with $\frac{1}{2}(\langle out|in\rangle) = \frac{1}{2}(\langle in|out\rangle)^*$

8 C_1 contributes with $\frac{1}{\sqrt{2}}$, while C_2 contributes with 1

In the following examples, I will clarify, hopefully, the meaning of these rules.

Figure 1– Diagrams over Molecular Orbitals. example 1

1– Sign $(-1)^{h+p+l\alpha+p\alpha} = (-1)^{1+0+1+0} = +$

2– No equivalent lines = 1

3– $(2)^{l\alpha+p\alpha} = (2)^{1+0} = 2$

4– No open lines = 1

5– $\langle i|\hat{F}|i\rangle = f_{ii}$

Hence thus diagram represents $2f_{ii}$

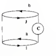

Figure 2: Diagrams over Molecular Orbitals example 2

1– Sign $(-1)^{h+p+l\alpha+l\beta}= (-1)^{2+0+2+0}= +$

2– $(\frac{1}{\sqrt{2}})^{\#\text{ of equivalent lines}}= (\frac{1}{\sqrt{2}})^{2}$

3– $(2)^{l\alpha+l\beta}=(2)^{2+0}$

4– $(\frac{1}{\sqrt{2}})^{p}=1$

6– $\frac{1}{2}(\langle out|in\rangle) = \frac{1}{2}(\langle ij|ab\rangle)$

7– $C_2 = 1$

Hence this diagram represents

$$+(\frac{1}{\sqrt{2}})^{2}\times(2)^{2}\times 1\times\frac{1}{2}(\langle ij|ab\rangle)C_{ij}^{ab} = (\langle ij|ab\rangle)C_{ij}^{ab} \qquad (133)$$

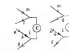

Figure 3. Diagrams over Molecular Orbitals example 3

The above diagrams clarify the concept of independent paths. One has to assign connected pairs such as (m, f), (n,g) for all double excitations associated with $\langle 0|S^f_m S^g_n(H-E)|\psi_g\rangle = 0$. For the left diagram the (m,f) and (n,g) pairs can be α or β spin independently: two independent α paths. The right diagram has only one independent α path because if (m,f) is α spin, then so is (n,g).

So the left diagram yields

$$(-1)^{1+2+0+2}(\frac{1}{\sqrt{2}})^0(2)^{2+0}(\frac{1}{\sqrt{2}})^2 f_{in} C^{fg}_{mi} = -2f_{in} C^{fg}_{mi} \qquad (134)$$

and the right diagram yields

$$(-1)^{1+2+0+1}(\frac{1}{\sqrt{2}})^0(2)^{1+0}(\frac{1}{\sqrt{2}})^2 f_{in} C^{fg}_{mi} = +f_{in} C^{fg}_{mi} \qquad (135)$$

CHAPTER 3
A PERTURBATION-VARIATIONAL METHOD FOR THE GROUND STATE

Introduction

The ground state potential energy surface is and has been subject of intense research over the years. A reliable description of the ground state at all internuclear distances is important to describe equilibrium geometries, rovibrational spectra, and the details of reactions.

In this chapter we revisit perturbation-variational theories [19, 91–94, 20–22, 23] and Brillouin-Wigner perturbation theory [84–86], that are capable of yielding a large fraction of the correlation energy rapidly and check the reliability of these methods in yielding the ground state correlation energy. Our extended goal in examining these methods is to obtain a balanced theory for molecular spectroscopy, and thus influences some of the ideas we present here.

In section 2, we present a non-iterative procedure for Brillouin-Wigner perturbation theory. In section 3, we analyze a variational method using a Krylov-type expansion and its connection to perturbation-variational procedures. In section 4 we present some of our results. Finally, in section 5, we summarize our results and present our conclusions.

Brillouin-Wigner Perturbation Theory

Remembering that the Resolvent is defined as

$$(\varepsilon - H_o)^{-1} Q = R \tag{136}$$

For Rayleigh-Schroedinger Perturbation Theory (RS) $\varepsilon = E_o$, and

$$R_{RS} = (E_o - H_o)^{-1} Q \tag{137}$$

For Brillouin Wigner Perturbation Theory (BW) $\varepsilon = E$, and

$$R_{BW} = R_{BW}(E) = (E - H_o)^{-1} Q \tag{138}$$

Remembering that

$$|\psi\rangle = \sum_{n=0}^{\infty} |\psi^{(n)}\rangle = \sum_{n=0}^{\infty} [R\, Q\, (V - E + \varepsilon)]^n |0\rangle \tag{139}$$

and

$$\begin{aligned} \Delta \mathrm{E} &= \sum_{n=1}^{\infty} E^n = \langle 0|V|\psi\rangle \\ &= \sum_{n=0}^{\infty} \langle 0|V\, [R\, Q\, (V - E + \varepsilon)]^n |0\rangle \end{aligned} \tag{140}$$

Assuming that ΔE is small by carefully partitioning the Hamiltonian, which is important and is discussed below, we rewrite the above expression as

$$\begin{aligned} R_{BW} - R_{RS} &= \left[\frac{-\Delta E}{(E_o - H_o)^2(1 + \frac{\Delta E}{(E_o - H_o)})}\right] Q \\ &= \frac{-\Delta E}{(E_o - H_o)^2} \sum_{n=0}^{\infty} \left[\frac{-\Delta E}{(E_o - H_o)}\right]^n Q \qquad (141) \\ &= \sum_{n=0}^{\infty} (-\Delta E)^{n+1} (R_{RS})^{n+2} \end{aligned}$$

thus

$$R_{BW} = \sum_{n=1}^{\infty} (-\Delta E)^{n-1} (R_{RS})^n \qquad (142)$$

hence

$$|BW^N\rangle = (R_{BW} V)^N |0\rangle = \left[\left(\sum_{n=1}^{\infty} (-\Delta E)^{n-1} (R_{RS})^n\right) V\right]^N |0\rangle \qquad (143)$$

and

$$E_{BW}^{N+1} = \langle 0|V|BW^N\rangle = \langle 0|V(R_{BW}V)^N|0\rangle = \langle 0|V\left[\left(\sum_{n=1}^{\infty} (-\Delta E)^{n-1} (R_{RS})^n\right) V\right]^N |0\rangle \qquad (144)$$

explicitly

$$E_{BW}^1 = E_{RS}^1 = \langle 0|V|0\rangle \qquad (145)$$

$$E_{BW}^2 = \sum_{n=1}^{\infty} (-1)^{n-1} (E_{BW}^1 + E_{BW}^2)^{n-1} \langle 0|V(R_{RS})^n V|0\rangle \qquad (146)$$

$$E_{BW}^3 = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-1)^{n+m-2} (E_{BW}^1 + E_{BW}^2 + E_{BW}^3)^{n+m-3} \langle 0|V(R_{RS})^n V(R_{RS})^m V|0\rangle \qquad (147)$$

$$E_{BW}^{4} = \sum_{k=1,l=1,m=1}^{\infty} (-\Delta E)^{k+l+m-3} \langle 0|V(R_{RS})^{k}V(R_{RS})^{l}V(R_{RS})^{m}V|0\rangle \tag{148}$$

$$E_{RS}^{2} = \langle 0|VR_{RS}V|0\rangle \tag{149}$$

$$E_{RS}^{3} = \langle 0|VR_{RS}VR_{RS}V|0\rangle - E_{RS}^{1}\langle 0|V(R_{RS})^{2}V|0\rangle \tag{150}$$

$$E_{RS}^{4} = \langle 0|VR_{RS}(V-\langle V\rangle)R_{RS}(V-\langle V\rangle)R_{RS}V|0\rangle - \langle 0|VR_{RS}V|0\rangle\langle 0|V(R_{RS})^{2}V|0\rangle \tag{151}$$

From equations 143 and 144, one can see that the evaluation of the Brillouin Wigner terms that appear from the use of expansion 142 are as difficult as the corresponding Rayleigh-Schroedinger terms, as long as the expansion 142 converges quickly.

We return now to the question of the Hamiltonian partitioning and examine the assumption that ΔE is small relative to all excitations energies in the "Q space

In the normal Møller-Plesset partitioning [38, 65, 69, 70, 89]

$$
\begin{aligned}
H_o^{MP} &= f_{pq} p^\dagger q \\
V^{MP} &= \frac{1}{4}\langle pq||rs\rangle p^\dagger q^\dagger sr - \langle pk||qk\rangle p^\dagger q \\
E^1_{MP} &= -\frac{1}{2}\langle kl||kl\rangle
\end{aligned}
\tag{152}
$$

In general E^1_{MP} is as large or larger than the total energy. However, we can introduce a constant shift

$$C = -\frac{1}{2}\langle kl||kl\rangle = E^1_{MP} \tag{153}$$

redefining H_o and V as

$$
\begin{aligned}
H_o &= H_o^{MP} + C \\
V &= V^{MP} - C
\end{aligned}
\tag{154}
$$

Using this choice, reminiscent of the Epstein Nesbet partitioning [47, 88] we have

$$
\begin{aligned}
E^0 &= E_{HF} \\
E^1 &= 0
\end{aligned}
\tag{155}
$$

Summarizing, using this partitioning, modified Rayleigh Schroedinger (MRS)

$$E^0_{MRS} = E^0_{RS} + E^1_{RS} = E_{HF} \tag{156}$$

$$E^1_{MRS} = 0 \tag{157}$$

$$E^2_{MRS} = \frac{1}{4}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} = E^2_{RS} \tag{158}$$

$$\begin{aligned}E^3_{MRS} = \frac{1}{8}&\frac{\langle ij||ab\rangle\langle ab||cd\rangle\langle cd||ij\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_i + \epsilon_j - \epsilon_c - \epsilon_d)}\\ &+ \frac{\langle ij||ab\rangle\langle kl||ij\rangle\langle ab||kl\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b)}\end{aligned} \tag{159}$$

$$+ \frac{\langle ij||ab\rangle\langle ak||ic\rangle\langle cb||kj\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_k + \epsilon_j - \epsilon_a - \epsilon_c)} = E^3_{RS}$$

$$E^N_{MRS} = E^N_{RS} \quad N > 1 \tag{160}$$

$$E^0_{MBW} = E^0_{RS} + E^1_{RS} = E_{HF} \tag{161}$$

$$E^1_{MBW} = 0 \tag{162}$$

$$E^2_{MBW} = \sum_{n=0}^{\infty}(-E^2_{MBW})^n \frac{1}{4}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{n+1}} = \sum_{n=0}^{\infty} a_n \left(E^2_{MBW}\right)^n \tag{163}$$

$$
\begin{aligned}
E^{3}_{MBW} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}(-E^{2}_{MBW} - E^{3}_{MBW})^{n+m}\{ \\
\frac{1}{8}\frac{\langle ij||ab\rangle\langle ab||cd\rangle\langle cd||ij\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)^{n+1}(\epsilon_i+\epsilon_j-\epsilon_c-\epsilon_d)^{m+1}} + \\
\frac{1}{8}\frac{\langle ij||ab\rangle\langle kl||ij\rangle\langle ab||kl\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)^{n+1}(\epsilon_k+\epsilon_l-\epsilon_a-\epsilon_b)^{m+1}} + \qquad (164) \\
\frac{\langle ij||ab\rangle\langle ak||ic\rangle\langle cb||kj\rangle}{(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)^{n+1}(\epsilon_k+\epsilon_l-\epsilon_a-\epsilon_b)^{m+1}}\} \\
= \sum_{n=0}^{\infty}\beta_n\,(E^{2}_{MBW} + E^{3}_{MBW})^{n}
\end{aligned}
$$

The term of lowest exponent in the Brillouin Wigner expansions (161–164) are just the corresponding Rayleigh-Schroedinger expressions (156–160)

One can estimate how fast the polynomial coefficients decrease by noting that $\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b \geq 2\,\delta$ where δ is the homo-lumo gap, leading to $\frac{a_{n+1}}{a_n} \sim \frac{\beta_{n+1}}{\beta_n} \sim \frac{-1}{2\,\delta}$ Hence in situations where the homo-lumo gap is not too small (near degeneracies) one can expect a quick convergence In other cases, quasi-degenerate theories should be used

Perturbation-Variational Theory

The inclusion of just a single variational parameter in front of the first order Rayleigh Schroedinger wavefunction proved to give very good results even in regions of the potential energy surface in which PT does not converge

The advantages of perturbation- variational methods are their far greater speed over conventional variational methods such as (matrix diagonalization) Configuration-Interaction (CI), and their far greater stability over Perturbation Theories for larger regions of the Potential Energy Surface. These methods however, are not size extensive leading to conflicting opinions on their utility [19, 91–96].

Using the approach of section 2, one can write the first order Brillouin-Wigner wavefunction as

$$|BW^1\rangle = \sum_{n=0}^{\infty}(-E_{BW})^n|n+1\rangle \tag{165}$$

where

$$\begin{aligned} |n\rangle &= (E_0 - H_0)^{-n} Q V^{MP}|0\rangle \\ &= (R_{RS})^n Q V^{MP}|0\rangle \\ &= |^{ab}_{ij}\rangle \frac{\langle ab||ij\rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^n} \end{aligned} \tag{166}$$

we examine the following approximation to the ground state wavefunction

$$|\psi\rangle = C_0|0\rangle + \sum_{n=1}^{NEXP} C_n|n\rangle \tag{167}$$

where the coefficients, $\{C_n\}$, are variational parameters and $NEXP$ is the number of the "expanded space functions".

This expansion is a Krylov-like expansion [97]. In the limit of $NEXP =$ number of double-excitations with the same symmetry as the ground state, it yields

CI-D However, near-linear dependencies appear well before the true theoretical linear dependency limit is approached

Near dissociation, where usually a few specific configuration become important, we also considered

$$|\psi\rangle = C_0|0\rangle + \sum_{n=1}^{NEXP} C_n|n\rangle + \sum_{\substack{k<l\\ c<d}} D_{kl}^{cd}|{}_{kl}^{cd}\rangle \tag{168}$$

where $P = |0\rangle\langle 0| + \sum_{\substack{k<l\\ c<d}} |{}_{kl}^{cd}\rangle\langle{}_{kl}^{cd}|$ and $|{}_{kl}^{cd}\rangle = c^\dagger d^\dagger lk|0\rangle$ is limited to a subspace of doubles important to describe the bond breaking. This, as expected, improves the accuracy and the numerical stability of the procedure, but at the cost of a modest amount of increased computer expense Below we prove the validity of using a sequence such as $\sum_n C_n|v_n\rangle = \sum_n C_n(\hat{A})^n|v\rangle$ in solving the Schroedinger equation

We wish to solve the eigenvalue problem

$$\begin{gathered} \hat{B}|b\rangle = \beta|b\rangle \\ \hat{B} = \hat{B}^\dagger \end{gathered} \tag{169}$$

assuming an appropriate $|b\rangle$ of the form given in equations 167 or 168 Let us consider the operator $\hat{A}$, and its non-degenerate eigenvalues and eigenvectors

$$\begin{gathered} \hat{A}|a_m\rangle = \alpha_m|a_m\rangle, \quad m = 1\ M \\ \hat{A} = \hat{A}^\dagger \end{gathered} \tag{170}$$

We construct a new basis set of the form

$$|v_n\rangle = (\hat{A})^n|v\rangle, \quad n = 1, N \tag{171}$$

and we will show that the set $\{|v_n\rangle\}_1^N$ is linear independent, i.e. $\sum_{n=1}^{N} \eta_n |v_n\rangle = 0 \Rightarrow \eta_n \equiv 0, \quad \forall n$

To prove this, we resolve $|v\rangle$ in $\{|a_m\rangle\}_1^M$ as $|v\rangle = \sum_{m=1}^{M} \zeta_m |a_m\rangle = \sum_{m=1}^{M} |a_m\rangle\langle a_m|v\rangle$

One obtains

$$\begin{aligned} 0 = \sum_{n=1}^{N} \eta_n |v_n\rangle &= \sum_{n=1}^{N} \eta_n (\hat{A})^n |v\rangle \\ &= \sum_{n=1}^{N} \eta_n (\hat{A})^n \sum_{m=1}^{M} \zeta_m |a_m\rangle \\ &= \sum_{n=1}^{N} \sum_{m=1}^{M} \eta_n \zeta_m (\alpha_m)^n |a_m\rangle \\ &= \sum_{m=1}^{M} \zeta_m |a_m\rangle \sum_{n=1}^{N} \eta_n (\alpha_m)^n \end{aligned} \tag{172}$$

$\sum_{n=1}^{N} \eta_n (\alpha_m)^n = \kappa_m$ is a number Thus $\sum_{m=1}^{M} \zeta_m \kappa_m |a_m\rangle = 0 \Rightarrow \zeta_m \kappa_m \equiv 0, \forall m$ since $\{|a_m\rangle\}_1^M$ is a linear independent.

For every $\zeta_m \neq 0$ we must have $\kappa_m = 0$ Let us assume we have $L \leq M$

such non-zero ζ_m, then

$$\sum_{n=1}^{N} \eta_n(\alpha_1)^n = 0$$

$$\vdots$$

$$\sum_{n=1}^{N} \eta_n(\alpha_i)^n = 0 \qquad (173)$$

$$\vdots$$

$$\sum_{n=1}^{N} \eta_n(\alpha_L)^n = 0$$

Thus if $N \leq L \Rightarrow \eta_n \equiv 0$, $\forall n$. So we can generate a linear independent set for the $N-$ dimensional space spanned by $\{|v_n\rangle\}_1^N = \{(A)^n|0\rangle\}_1^N$.

In this space we want to solve $(\hat{B} - \beta\hat{1})|b\rangle = 0$. Expanding

$$|b\rangle = \sum_{n=1}^{N} \mu_n |v_n\rangle \qquad (174)$$

we obtain in standard fashion

$$det(B_{kl} - b\, S_{kl}) = 0 \qquad (175)$$

where

$$\begin{aligned} B_{kl} &= \langle v_k|B|v_l\rangle \\ S_{kl} &= \langle v_k|v_l\rangle \end{aligned} \qquad (176)$$

In our present case $|v\rangle = Q\, V^{MP}|0\rangle$ and $\hat{A} = R_{RS} = (E_o - H_o)^{-1}Q$, so $\{|v_n\rangle\} = \{|n\rangle\} = \{(R_{RS})^n Q\, V^{MP}|0\rangle\}$, which expands the double excited space of same symmetry as the reference function

Results

All the calculations were performed using INDO/1 Model Hamiltonian [81 82] and minimum basis set. All results are shown in atomic units, unless explicitly said otherwise.

In tables 3–7 , we show the 2nd and 3rd order Brillouin-Wigner results using the expansions described in section 2, for water, methane, formaldehyde, acethylene, and benzene near the experimental equilibrium geometries N_{max} is the order of polynomial in the right hand side of equation 162 One sees that the series quickly converges The percent error is with respect to the larger CI calculation we performed , in general CI Full

We also, can see the importance in choosing the constant C The second column shows results for E^{2}_{BW} when $C = 0$, while the third column shows them for E^{1}_{BW} when $C = -\frac{1}{2}\langle kl||kl\rangle$ When $C = 0$ $V = V^{MP}$, the sequence is not convergent. In all the cases examined the zeroth iteration, the RS result, is closer to the CI Full result. In the case of benzene, we do not have the CI Full result. The toughest case was benzene, which took a polynomial of 7 th degree however, it is still a easy task

Table 3 H_2O — Brillouin-Wigner Results

	H_2O [a]	E_{HF}= -18.120732	$\Delta E_{CI\text{-}D}$= -.038530 (2%)	$\Delta E_{CI\text{-}Full}$= -.039185
N_{max}	E^2_{BW} $(V = V^{MP})$	E^2_{BW}	E^3_{BW}	$E^2_{BW} + E^3_{BW}$
0 (RSPT)	-.026250	-.026250	-.008457	-.034707 (11%)
1	-.214201	-.025990	-.008229	-.034219
2	-1.42935	-.025993	-.008234	-.034227 (13%)

a) d_{HO}=1.0130 Å θ_{HOH}=104.5230°

Table 4 CH_4 — Brillouin-Wigner Results

	CH_4 [a]	E_{HF}= 9.260282	$\Delta E_{CI\text{-}D}$= -.042860 (2%)	$\Delta E_{CI\text{-}Full}$= -.043689
N_{max}	E^2_{BW} $(V = V^{MP})$	E^2_{BW}	E^3_{BW}	$E^2_{BW} + E^3_{BW}$
0 (RSPT)	-.029022	-.029022	-.009682	-.038704 (11%)
1	-.171979	-.028700	-.009391	-.038091
2	-.812863	-.028703	-.009397	-.038100 (13%)

a) d_{CH}=1.0550 Å, θ_{HCH}=109.47°

Table 5 H_2CO — Brillouin Wigner Results

	H_2CO [a]	E_{HF}= -24.441506	$\Delta E_{CI\text{-}D}$= -.100381 (6%)	$\Delta E_{CI\text{-}Full}$= -.106545
N_{max}	E^2_{BW} $(V = V^{MP})$	E^2_{BW}	E^3_{BW}	$E^2_{BW} + E^3_{BW}$
0 (RSPT)	-080365	-080365	-015918	-096283 (10%)
1	-1.30409	-077366	-014250	-.091616
2	-10.9855	-077487	-014394	-091881
3	-21.5074	-077482	-014382	-091864 (14%)

a) d_{CH}=1.0990 Å, d_{CO}=1.203 Å, θ_{HCH}=121.75°

Table 6 C_2H_2 — Brillouin Wigner Results

	C_2H_2 [a]	E_{HF}= -13.574992	$\Delta E_{CI\text{-}D}$= -.103317 (7%)	$\Delta E_{CI\text{-}Full}$= -.111199
N_{max}	E^2_{BW} $(V = V^{MP})$	E^2_{BW}	E^3_{BW}	$E^2_{BW} + E^3_{BW}$
0 (RSPT)	-089220	-089220	-012832	-102052 (8%)
1	-839939	-085128	-011383	-096511
2	-5.29892	-085324	-011517	-096841
3	-10.8770	-085314	-011505	-096819
4	-13.6370		-011506	-096820 (13%)

a) d_{CC}=1.2024 Å, d_{CH}=1.0750 Å, linear

Table 7 C_6 H_6 — Brillouin Wigner Results

	C_6H_6 [a]	E_{HF}= -40.020138	ΔE_{CI-D}= -.300456 (2%)	ΔE_{CI-SDT}= -.305492
N_{max}	E^2_{BW} $(V = V^{MP})$	E^2_{BW}	E^3_{BW}	$E^2_{BW} + E^3_{BW}$
0 (RSPT)	-.294946	-.294946	-.039503	-.334449 (9%)
1	-18.3999	-.251100	-.027185	-.278285
2	-94.51140	-.257752	-.030552	-.2883304
3	-111.791	-.256403	-.029527	-.285930
4	-116.155	-.256689	-.029858	-.286547
5	-117.904	-.256623	-.029744	-.286367
6	-118.802	-.256639	-.029784	-.286423
7	-119.336	-.256635	-.029770	-.286405 (6%)

a) d_{CC}=1.4000 Å d_{CH}=1.0880 Å

In table 8 , we can see that the variational procedure described in section 3 soon saturates. With the exception of CH_4, all other cases shows instabilities when the lowest and largest eigenvalues of the overlap matrix S is of order 10^{-12}. Since increasing the basis set must monotonically decrease the energy, any increase is an indication of numerical problems. From observation, the inclusion of 5 expanded functions (NEXP=5) seems to give good and reliable results at all internuclear separations. The theoretical limit is, of course, CID, and the error from the theoretical limit is lower than 10% at all internuclear distances. The computational effort is the same as 3rd order Perturbation Theory

Table 8 Perturbation – Variational Results

	H_2O [a]	CH_4 [b]	H_2CO [c]	C_2H_2 [d]	C_6H_6 [e]
NEXP=1	-037920	- 042502	-094809	098146	-285025
NEXP=2	-038126	-042669	-096147	-098221	-.287051
NEXP=3	038170	042686	096704	098238	-.287076
NEXP=4	038174	042724	097165	098404	-287198
NEXP=5	038177	042726	- 097625	098628	- 287241
NEXP=6	**-038177**	-042726	**- 097700**	- 098640	-.287272
NEXP=7	*038191*	- 042726	*-097905*	**- 099055**	-287305
NEXP=8	*038188*	-042726	*097885*	*099060*	- 287610
NEXP=9		042727		*099054*	-.287714
NEXP=10		042727			- 287916
NEXP=11		-042728			**-.287916**
NEXP=12		**- 042728**			*Linear Dependence*
E_{HF}	18 120732	-9 260282	24 441506	13 574992	-40 020138
$\Delta E_{CI/D}$	038530	042860	100381	103317	- 300456
ERROR	0 9 %	0 3 %	2 0 %	4 0 %	5 0 %

a) d_{HO}=1 0130 Å, θ_{HOH}=104.5230°

b) d_{CH}=1 0550 Å, θ_{HCH}=109 47°

c) d_{CH}=1 0990 Å d_{CO}=1 203 Å, θ_{HCH}=121 75°

d) d_{CC}=1 2024 Å d_{CH}=1 0750 Å, linear

e) d_{CC}=1 4000 Å d_{CH}=1 0880 Å

Table 9: H_2O symmetric stretch, θ_{HOH}=104.5230°

	d_{OH}	k
E_{HF}	1.882 (1 %)	2.58 (12 %)
E^2_{BS}	1.898 (0.4 %)	2.42 (5 %)
$E^2_{BS} + E^3_{BS}$	1.903 (0.2 %)	2.41 (4 %)
E^2_{BW}	1.897 (0.5 %)	2.38 (3 %)
$E^2_{BW} + E^3_{BW}$	1.903 (0.2 %)	2.46 (6 %)
NEXP5	1.905 (0.05 %)	2.36 (2 %)
NEXP5-S	1.905 (0.05%)	2.36 (2 %)
CI-D	1.905 (0.05 %)	2.40 (4 %)
CI-SD	1.905 (0.05 %)	2.36 (2 %)
CI-Full	1.906	2.31

Table 10 H_2CO θ_{HCH}=109.47°

	d_{CO}	k
E_{HF}	2.448 (2%)	1.97 (17%)
E^2_{BS}	2.502 (0.1%)	1.59 (5%)
$E^2_{BS} + E^3_{BS}$	2.500 (0.2%)	1.64 (2%)
E^2_{BW}	2.495 (0.4%)	1.64 (2%)
$E^2_{BW} + E^3_{BW}$	2.491 (0.6%)	1.87 (11%)
NEXP=5	2.492 (0.6%)	1.75 (4%)
CI-D	2.495 (0.4%)	1.76 (5%)
CI-Full	2.506	1.68

Table 11 C_2H_2, d_{CH}=1.0750 Å, linear

	d_{CC}	k
E_{HF}	2.464 (3%)	1.80 (22%)
E^2_{RS}	2.549 (0.5%)	1.36 (8%)
$E^2_{RS} + E^3_{RS}$	2.525 (0.4%)	1.60 (8%)
E^2_{BW}	2.535 (0.04%)	1.52 (3%)
$E^2_{BW} + E^3_{BW}$	2.515 (0.8%)	1.72 (16%)
NEXP=5	2.514 (0.9%)	1.60 (8%)
CI-D	2.520 (0.6%)	1.56 (5%)
CI Full	2.536	1.48

In tables 9–11, we show the calculated geometries and force constants for water, methane, formaldehyde and acetylene, and its comparison to the CI-Full result. 2nd-order Brillouin-Wigner seems to give better results than 2nd order Rayleigh Schroedinger for bond length and force constant. Our variational method results are very close to CID, but, again, at a function of the computer cost.

Figures 4–6 show the symmetrical stretch curve for water at a fixed angle θ_{HOH}=104.52°. One can see from figure 5, that around equilibrium all approximations are fairly good. At long distances (d_{HO}> 4.0 bohr) Rayleigh Schroedinger perturbation theory breaks down expected (figure 4), but around the minimum the Brillouin- Wigner results closely follow the Rayleigh Schroedinger results. Using our proposed expansion, we were able to obtain results for Brillouin-Wigner perturbation theory up to d_{HO}= 3.5 bohr. NEXP=5 (NEXP5) follows closely the results obtained for the most computational demanding CID, and CI-Full. Better agreement is obtained when singles are included (NEXP5S) since the bond breaking mainly involves both double and single excitations. One also can see that NEXP5 is stable even when Perturbation Theory breaks down again as expected.

Figure 7 shows the breaking of the double bond of formaldehyde using the different perturbation theories, second order Brillouin- Wigner and third order Rayleigh- Schroedinger yields the same force constants (table 10), which is in better agreement with the full-CI results. In figure 8, we see an artificial maximum which appear for CID. This is absent in NEXP5, but reappears in NEXP=5 + CID over a restricted space spanned by double excitation from occupied orbital (4–6) to virtual orbitals (7–8) (NEXP5_48). It should be noted that in the dissociation limit (6.5 bohr) CID over this restricted space (CI-D_48) and NEXP5_48 present an error with respect to CID of .004% while NEXP5 presents .2%. On the other hand, near the equilibrium geometry (2.495 bohr) CI-D_48 has an error of .2% while NEXP5 and NEXP5_48 have only a .01% error with respect to CID. Hence NEXP5_48 seems to follow closely the CID curve at all internuclear distances. The inclusion of single excitations, figure 9, removes the artificial maximum in all cases. Quadrupoles excitations do not seem to be important in this case.

Figure 10 and 11 show the breaking of acethylene's triple bond. Perturbation Theory breaks down very early (figure 7), and at d_{CC}> 3.0 bohr, we can no longer make our expansion for Brillouin-Wigner perturbation theory converge. Near the minimum Brillouin-Wigner results seem better behaved (see Figure 10 and table 11). Perhaps this is due to the fact that 3rd-order Brillouin-Wigner results are upper bounds, suggesting an easy and cheap way to evaluate the reliability of perturbation theory results. However, unlike Rayleigh-Schroedinger perturbation theory, it is not a size-extensive theory.

NEXP5 follows CID closely. NEXP5_48 (NEXP5 + CID over a restricted space spanned by double excitation from occupied orbital (4–6) to virtual orbitals (7–8)) gives very good results. Again, the error in the correlation energy expanded by CID is 0.1% for CI-D_38, 0.4% for NEXP5, 0.1% for NEXP5_48 at large internuclear distances (4.5 a.u.), and, respectively, 0.3%, 0.05%, and 0.02% near the equilibrium position (2.515 a.u.). Quadrupoles excitations are important and are responsible for the disagreement between CID and CI Full.

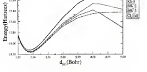

Figure 4 H_2O — Perturbation Theory

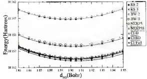

Figure 5 H_2O — Near Equilibrium

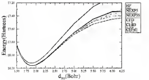

Figure 6 H_2O

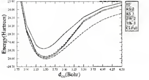

Figure 7 CH_2O — Perturbation Theory

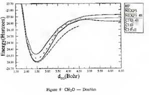

Figure 8 CH_2O — Doubles

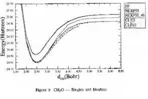

Figure 9 CH_2O — Singles and Doubles

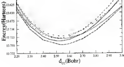

Figure 10: C_2H_2 — Perturbation Theory

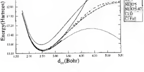

Figure 11: C_2H_2

Summary and Conclusions

We have described a simple expansion of the Krylov type and have used it to derive energy expressions for Brillouin Wigner perturbation theory from Rayleigh Schroendinger perturbation theory as well as define a variation-perturbation procedure using a reduced space of double excitations, thus a "reduced space method"

Brillouin-Wigner perturbation theory calculations take very little additional time over the Rayleigh-Schroendinger perturbation theory calculations In the examples we reported here and others not reported third order Rayleigh Schroendinger theory recaptures more of the correlation energy than does Brillouin Wigner theory, but force constants and bond distances are better reproduced using second order Brillouin Wigner perturbation theory

The reduced space variational procedure NEXP5 follows CID closely over all regions of the potential energy surface in the cases examined here, the difference in the correlation energy is less than 7% Variational NEXP5_CID follows CID closer but with increased computational cost, NEXP5S theory that includes single excitations seems quite accurate when compared with CI-Full, and it is thus quite efficient theory that we now examine for electronic spectroscopy

CHAPTER 4
FREQUENCY INDEPENDENT RESPONSE PROPERTIES

Introduction

We investigate nature through the response of a system to some external factor. One of the most common probes is a static electric field (E). Let us investigate [65] the response of a state $|\psi\rangle$ corresponding to $\mathbf{H}$ to an external time-independent one-electron perturbation $\lambda\mathbf{H}_1$.

We consider the effect on the energy of

$$\mathbf{H} \rightarrow \mathbf{H} + \lambda\mathbf{H}_1 \tag{177}$$

Such perturbations make the total electronic energy a function of λ and may be expanded, for small λ, in a power series

$$E(\lambda) = \langle\psi|H + \lambda H_1|\psi\rangle = E_0 + \lambda E_1 + \frac{1}{2}\lambda^2 E_2 + \frac{1}{6}\lambda^3 E_3 + \tag{178}$$

The terms that are nonlinear in λ arise because the state wavefunction $|\psi\rangle$ depends on λ, or has "responded" to the perturbation. When, for example, $\lambda\mathbf{H}_1$ represents a static electric field ($\lambda\mathbf{H}_1 = \mathbf{E}\cdot\mathbf{r}$), E_1 yields the permanent electric dipole moment (μ) of the unperturbed state $|\psi\rangle$, E_2 gives the state's polarizability (α), and E_3, E_4 etc. yield higher hyperpolarizabilities (β, γ,etc.)

The presence of an electric field can dramatically change the molecular orbitals of the system. The inclusion of the single excitation manifold does not change the zero order energy, but its presence allows us to account for the orbital relaxation due to the field. However, the calculation of properties is often more sensitive to the quality of the wave function than the energy, so the use of a correlated zero order energy seems appropriated.

We propose two ways to accomplish the inclusion of relaxation and correlation in the calculation of dipole moment and polarizability. The first is reminiscent of a CC-S applied to a correlated reference function. The second can be viewed as a linearized CC-S, or more appropriately a Tamm-Dancoff Approximation (TDA) or CI-S on a correlated reference function.

In section 2, we present a short review on CC response properties. In section 3, we introduce our modified CC-S and CI-S response properties. Finally we summarize our results and present our conclusions in section 4.

The Coupled-Cluster Response Properties [65, 98]

Assuming that the Hamiltonian can be written as

$$H(\lambda) = H + \lambda H_1 \tag{179}$$

and the wave operator

$$\Omega(\lambda) = \exp[T(\lambda)] \tag{180}$$

i.e. the wavefunction can be expressed as

$$|\psi(\lambda)\rangle = \Omega(\lambda)|0\rangle \tag{181}$$

then

$$\exp[-T(\lambda)]H(\lambda)\exp[T(\lambda)]|0\rangle = E(\lambda)|0\rangle \tag{182}$$

Neglecting the variations in the orbitals when the field is applied, the equations for the energy and cluster amplitudes become

$$\langle 0|\exp[-T(\lambda)]H(\lambda)\exp[T(\lambda)]|0\rangle = E(\lambda) \tag{183}$$

and

$$\langle {}^{abc}_{ijk} \,|\exp[-T(\lambda)]H(\lambda)\exp[T(\lambda)]|0\rangle = 0 \tag{184}$$

The above Hamiltonian can be expanded in powers of the field λ once the cluster operator $T(\lambda)$ and $H(\lambda)$ are so expanded

$$T(\lambda) = T^{0} + \lambda T^{(1)} + \lambda^2 T^{(2)} + \tag{185}$$

$$E(\lambda) = E^{0} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \tag{186}$$

The resultant first- and second-order equations are

$$E^{(1)} = \langle 0|\exp[-T^{0}]\{H_1 + [H, T^{(1)}]\}\exp[T^{0}]|0\rangle \qquad (187)$$

$$0 = \langle {}^{abc}_{ijk}|\exp[-T^{0}]\{H_1 + [H, T^{(1)}]\}\exp[T^{0}]|0\rangle \qquad (188)$$

and

$$E^{(2)} = \langle 0|\exp[-T^{0}]\{[H_1, T^{(1)}] + \frac{1}{2}[[H, T^{(1)}], T^{(1)}] + [H, T^{(2)}]\}\exp[T^{0}]|0\rangle \quad (189)$$

$$0 = \langle {}^{abc}_{ijk}|\exp[-T^{0}]\{[H_1, T^{(1)}] + \frac{1}{2}[[H, T^{(1)}], T^{(1)}] + [H, T^{(2)}]\}\exp[T^{0}]|0\rangle \quad (190)$$

Dipole Moment and Polarizability

Within the CI framework, the dipole moment is just an expectation value of the ground state, hence the dipole moment calculation is a direct measure of how "good" the wavefunction is. On the other hand, one can view the expectation value of the one electron operator as a sum of the overlap between the CI wavefunction and a function which includes single excitations and de-excitations with respect to the CI ground state. Coupled Hartree-Fock (CHF) or Random Phase Approximation (RPA) needs only single and double excitations to describe dipole moment and polarizability.

Oddershede and Svendsen [99] have shown that the polarizability tensor is well described within the CHF approximation Öhrn et al [100] have observed that the extension of RPA and TDA to a correlated reference function results in similar results for transition energies and transition moments Thus we propose to use a wavefunction that is a combination of single excitations on a correlated reference function

The first method is similar to a Coupled Cluster Singles (CC-S) applied to a first order perturbation theory reference function or a perturbation-variational function

The second method can be viewed as a linearized CC-S where only the terms depending linearly of the cluster amplitudes are retained This method can also be interpreted as a generalized Tamm-Dancoff Approximation, or CI-S where the reference function is corrected to first order in perturbation theory, or is obtained through a perturbation-variational procedure

Both methods are solved requiring that the Schroedinger equation be obeyed in the subspace spanned by the Hartree-Fock wavefunctions and its single excited configurations

Explicitly, one has

Modified CC-S

$$|\psi_a\rangle = |0\rangle + |1\rangle$$

$$|1\rangle = RV|0\rangle$$

$$E^{2}_{PT} = \langle 0|V|1\rangle = \langle 0|VRV|0\rangle$$

$$R = \frac{\hat{Q}}{(\epsilon - H_o)} \begin{cases} \epsilon = E_a & RSPT \\ \epsilon = E & BWPT \end{cases}$$

$$\hat{Q} = \hat{1} - |0\rangle\langle 0| - |^{a}_{i}\rangle\langle^{a}_{i}| \qquad (191)$$

$$H_o = f_{pq} p^{\dagger} q$$

$$V = \langle pq||rs\rangle p^{\dagger} q^{\dagger} sr - \langle pk||qk\rangle p^{\dagger} q$$

$$|\psi\rangle = e^{T_1}|\psi_a\rangle \quad T_1 = t^{a}_{i} a^{\dagger} i$$

$$|^{a}_{i}1\rangle = a^{\dagger} i|1\rangle$$

Response Properties

Assuming $H_1 = \vec{E}\,\langle p|\vec{r}|q\rangle\, p^{\dagger} q$ is an one electron operator

$$\begin{aligned} H(\lambda) &= H + \lambda\, H_1 \\ \exp[-T_1(\lambda)]H(\lambda)\exp[T_1(\lambda)]|\psi_a\rangle &= E(\lambda)|\psi_a\rangle \\ T_1(\lambda) &= T_1^{(0)} + \lambda T_1^{(1)} + \lambda^2 T_1^{(2)} + \\ E(\lambda) &= E^{(0)} + \lambda\, E^{(1)} + \lambda^2\, E^{(2)} + \end{aligned} \qquad (192)$$

1

$$E^{(0)} = \langle 0|e^{-T_1^{(0)}} H e^{T_1^{(0)}}|\psi_a\rangle \qquad (193)$$

$$\langle {}^{b}_{j}| e^{-T_1^{(0)}} H e^{T_1^{(0)}} |\psi\rangle = 0 \tag{194}$$

a.

$$E^{(0)} = E_{HF} + E^{2}_{PT} + t_i^{a(0)} f_{ia} + \frac{1}{2} t_i^{a(0)} t_j^{b(0)} \langle ij||ab\rangle \tag{195}$$

b

$$\begin{gathered} E^{2}_{PT}\, t_j^{b(0)} = f_{bj} + \langle {}^{b}_{j}|H|1\rangle + \\ t_j^{a(0)} f_{ba} - t_i^{b(0)} f_{ij} - t_j^{a(0)} t_i^{b(0)} f_{ia} + t_i^{a(0)} \langle bi||ja\rangle + \\ t_i^{c(0)} \Big\{ \langle {}^{b}_{j}|H|{}^{c}_{i} 1\rangle + t_k^{b(0)} \langle ik||aj\rangle - t_j^{c(0)} \langle bi||ca\rangle - t_j^{c(0)} t_k^{b(0)} \langle ik||ac\rangle \Big\} \end{gathered} \tag{196}$$

2.

$$E^{(1)} = \langle 0| e^{-T^{(0)}} \Big\{ H_1 + \Big[H, T^{(1)}\Big] \Big\} e^{T^{(0)}} |\psi_0\rangle \tag{197}$$

$$\langle {}^{b}_{j}| e^{-T^{(0)}} \Big\{ H_1 + \Big[H, T^{(1)}\Big] \Big\} e^{T^{(0)}} |\psi_0\rangle = 0 \tag{198}$$

a.

$$\begin{gathered} E^{(1)} = \langle 0|H_1|0\rangle + \langle 0|H_1|{}^{a}_{i}\rangle\, t_i^{a(0)} + \\ f_{ia}\, t_i^{a(1)} + \langle ij||ab\rangle t_i^{a(1)} t_j^{b(0)} \end{gathered} \tag{199}$$

b

$$\begin{gathered} E^{(0)}\, t_j^{b(1)} = -E^{(1)}\, t_j^{b(1)} \\ \langle{}^{b}_{j}|H_1|0\rangle + \langle{}^{b}_{j}|H_1|1\rangle + \\ \langle{}^{b}_{j}|H_1|{}^{a}_{i}\rangle\, t_i^{a(0)} + \\ [\langle{}^{b}_{j}|H|{}^{a}_{i}\rangle + \langle{}^{b}_{j}|H|{}^{a}_{i}\ 1\rangle]\, t_i^{a(1)} + \\ \frac{1}{2}\langle{}^{b}_{j}|H_1|{}^{ac}_{ik}\rangle\, t_i^{a(0)} t_k^{c(0)} + \\ \langle{}^{b}_{j}|H|{}^{ac}_{ik}\rangle\, t_i^{a(1)} t_k^{c(0)} + \frac{1}{2}\langle{}^{b}_{j}|H|{}^{acd}_{ikl}\rangle\, t_i^{c(1)} t_k^{c(0)} t_l^{d(0)} \end{gathered} \tag{200}$$

$$E^{(2)} = \langle 0|e^{-T^{(0)}}\left\{[H_1, T^{(1)}] + \frac{1}{2}[[H_1, T^{(1)}], T^{(1)}] + [H\ T^{(2)}]\right\} e^{T^{(0)}}\,|\psi_0\rangle \tag{201}$$

$$\langle{}^{b}_{j}|e^{-T^{(0)}}\left\{[H_1\ T^{(1)}] + \frac{1}{2}[[H_1, T^{(1)}], T^{(1)}] + [H\ T^{(2)}]\right\} e^{T^{(0)}}\,|\psi_0\rangle = 0 \tag{202}$$

a

$$\begin{gathered} E^{(2)} = \langle 0|H_1|{}^{a}_{i}\rangle\, t_i^{a(1)} + f_{ia}\, t_i^{a(2)} + \\ \langle ij||ab\rangle [t_i^{a(2)} t_j^{b(0)} + \frac{1}{2} t_i^{a(1)} t_j^{b(1)}] \end{gathered} \tag{203}$$

$$
\begin{aligned}
E^{(0)}\, t_j^{b(2)} = -E^{(2)}\, t_j^{b(0)} - E^{(1)}\, t_j^{b(1)} + \\
\langle {}^{b}_{j}|H_1|{}^{a}_{i}\rangle\, t_i^{a(1)} + \\
[\langle {}^{b}_{j}|H|{}^{a}_{i}\rangle + \langle {}^{b}_{j}|H|{}^{a}_{i}, 1\rangle]\, t_i^{a(2)} + \\
\langle {}^{b}_{j}|H_1|{}^{ac}_{ik}\rangle\, t_i^{a(1)} t_k^{c(0)} + \\
\langle {}^{b}_{j}|H|{}^{ac}_{ik}\rangle\, t_i^{a(1)} t_k^{c(1)} + \langle {}^{b}_{j}|H|{}^{acd}_{ikl}\rangle\, t_i^{a(0)} t_k^{c(1)} t_l^{d(1)} + \\
t_i^{a(2)} (\langle {}^{b}_{j}|H|{}^{ac}_{ik}\rangle\, t_k^{c(0)} + \langle {}^{b}_{j}|H|{}^{acd}_{ikl}\rangle\, t_k^{c(0)} t_l^{d(0)})
\end{aligned}
\tag{204}
$$

The appearance of terms connecting singles with doubles and triples makes this approximated method not very attractive. The linear terms in the cluster amplitudes, on the other hand, have the signature that we are looking for. So we introduce the Modified CI-S.

Modified CI-S

Similarly to the Modified CC-S, we define

$$
\begin{gathered}
|\psi_o\rangle = |0\rangle + |1\rangle \\
|1\rangle = RV|0\rangle \\
E^2_{PT} = \langle 0|V|1\rangle = \langle 0|VRV|0\rangle \\
R = \frac{\hat{Q}}{(\varepsilon - H_o)} \begin{cases} \varepsilon = E_o & RSPT \\ \varepsilon = E^{(0)} & BW\ PT \end{cases} \\
\hat{Q} = 1 - |0\rangle\langle 0| - |^{a}_{i}\rangle\langle^{a}_{i}| \\
H_o = f_{pq} p^\dagger q \\
V = \langle pq||rs\rangle p^\dagger q^\dagger sr - \langle pk||qk\rangle p^\dagger q \\
|\psi\rangle = (1 + C_1)|\psi_o\rangle \\
C_1 = C^a_i a^\dagger i \\
|^{a}_{i}\ 1\rangle = a^\dagger i|1\rangle
\end{gathered}
\tag{205}
$$

$$
\begin{gathered}
H(\lambda) = H + \lambda\ H_1 \\
H(\lambda)(1 + C_1(\lambda))|\psi_o\rangle = E(\lambda)(1 + C_1(\lambda))|\psi_o\rangle \\
C_1(\lambda) = C^{(0)} + \lambda C^{(1)} + \lambda^2 C^{(2)} + \\
E(\lambda) = E^{(0)} + \lambda\ E^{(1)} + \lambda^2\ E^{(2)} +
\end{gathered}
\tag{206}
$$

Collecting all terms of same order, one obtains.

$$\lambda^0 \quad [H - E^{(0)}][1 + C_1^{(0)}]|\psi_o\rangle = 0$$

$$\lambda^1 \quad [H - E^{(0)}]C_1^{(1)}|\psi_o\rangle = -[H_1 - E^{(1)}][1 + C_1^{(0)}]|\psi_o\rangle$$

$$\lambda^2 \quad [H - E^{(0)}]C_1^{(2)}|\psi_o\rangle = -[H_1 - E^{(1)}]\, C_1^{(1)}|\psi_o\rangle + E^{(2)}[1 + C_1^{(0)}]|\psi_o\rangle$$

$$\lambda^3 \quad [H - E^{(0)}]C_1^{(3)}|\psi_o\rangle = -[H_1 - E^{(1)}]\, C_1^{(2)}|\psi_o\rangle +$$

$$E^{(2)}C_1^{(1)}|\psi_o\rangle + E^{(3)}[1 + C_1^{(0)}]|\psi_o\rangle \tag{207}$$

One can obtain the equations for $\{C_1^{(n)}\}$ and $\{E^{(n)}\}$ by projecting in the space spanned by $|0\rangle$ and $\{|{}^a_i\rangle\}$. Explicitly.

$$E^{(0)} = E_{HF} + E^{(2)}_{PT} + C_i^{a(0)} f_{ia} \tag{208}$$

$$\begin{aligned} E^{(0)}C_j^{b(0)} = & \langle{}^b_j|H|0\rangle (= f_{bj}) + \langle{}^b_j|H|1\rangle + \\ & C_i^{a(0)}\{\langle{}^b_j|H|{}^a_i\rangle + \langle{}^b_j|H|{}^a_i\,1\rangle\} \end{aligned} \tag{209}$$

$$E^{(1)} = \langle 0|H_1|0\rangle + C_i^{a(0)}\langle 0|H_1|{}^a_i\rangle + C_i^{a(1)} f_{ia} \tag{210}$$

$$\begin{aligned} E^{(0)}C_j^{b(1)} = & -E^{(1)}C_j^{b(0)} + \\ & \langle{}^b_j|H_1|0\rangle + \langle{}^b_j|H_1|1\rangle + \\ & C_i^{a(0)}\langle{}^b_j|H_1|{}^a_i\rangle + \\ & C_i^{a(1)}\{\langle{}^b_j|H|{}^a_i\rangle + \langle{}^b_j|H|{}^a_i\,1\rangle\} \end{aligned} \tag{211}$$

$$E^{(2)} = C_i^{a(1)} \langle 0|H_1|{}^{a}_{i}\rangle + C_i^{a(2)} f_{ia} \tag{212}$$

$$\begin{aligned} E^{(0)} C_j^{b(2)} = & - E^{(1)} C_j^{b(1)} - E^{(2)} C_j^{b(0)} + \\ & C_i^{a(1)} \langle {}^{b}_{j}|H_1|{}^{a}_{i}\rangle + \\ & C_i^{a(2)} \{ \langle {}^{b}_{j}|H|{}^{a}_{i}\rangle + \langle {}^{b}_{j}|H|{}^{a}_{i}, 1\rangle \} \end{aligned} \tag{213}$$

$$E^{(3)} = C_i^{a(2)} \langle 0|H_1|{}^{a}_{i}\rangle + C_i^{a(3)} f_{ia} \tag{214}$$

$$\begin{aligned} E^{(0)} C_j^{b(3)} = & - E^{(1)} C_j^{b(2)} - E^{(2)} C_j^{b(1)} - E^{(3)} C_j^{b(0)} + \\ & C_i^{a(2)} \langle {}^{b}_{j}|H_1|{}^{a}_{i}\rangle + \\ & C_i^{a(3)} \{ \langle {}^{b}_{j}|H|{}^{a}_{i}\rangle + \langle {}^{b}_{j}|H|{}^{a}_{i}\ 1\rangle \} \end{aligned} \tag{215}$$

Specifically, one obtain for the dipole moment in the direction $\hat{e}_i$

$$\mu_i = \langle 0|x_i|0\rangle + \langle 0|x_i|{}^{a}_{i}\rangle \, C_i^{a(0)} \tag{216}$$

and for the component i,j of the polarizability

$$\alpha_{ij} = \frac{\partial C_i^{a(1)}}{\partial E_j} \langle 0|x_i|{}^{a}_{i}\rangle + \frac{\partial C_i^{a(1)}}{\partial E_i} \langle 0|x_j|{}^{a}_{i}\rangle \tag{217}$$

and for the component i,j,k of the hyperpolarizability

$$\beta_{ijk} = \frac{\partial^2 C_i^{a(2)}}{\partial E_i \partial E_j} \langle 0|x_k|{}^{a}_{i}\rangle + \frac{\partial^2 C_i^{a(2)}}{\partial E_i \partial E_k} \langle 0|x_j|{}^{a}_{i}\rangle + \frac{\partial^2 C_i^{a(2)}}{\partial E_j \partial E_k} \langle 0|x_i|{}^{a}_{i}\rangle \tag{218}$$

where E_i, E_j, E_k are the fields in the directions $\hat{e}_i$, $\hat{e}_j$ and $\hat{e}_k$, respectively

Hence we need only to solve for

$$E^{(0)} = E_{HF} + E_{PT}^{2} \tag{219}$$

$$E^{(0)} C_k^{c(0)} = \langle {}^{c}_{k} | H | 1 \rangle + \{ \langle {}^{c}_{k} | H | {}^{d}_{l} \rangle + \langle {}^{c}_{k} | H | {}^{d}_{l}, 1 \rangle \} C_l^{d(0)} \tag{220}$$

$$\begin{aligned} E^{(0)} \frac{\partial C_k^{c(1)}}{\partial E_i} = & - \mu_i C_k^{c(0)} + \\ & \langle {}^{c}_{k} | x_i | 0 \rangle + \langle {}^{c}_{k} | x_i | 1 \rangle + \\ & \langle {}^{c}_{k} | x_i | {}^{d}_{l} \rangle \; C_l^{d(0)} + \\ & \{ \langle {}^{c}_{k} | H | {}^{d}_{l} \rangle + \langle {}^{c}_{k} | H | {}^{d}_{l}, 1 \rangle \} \frac{\partial C_l^{d(1)}}{\partial E_i} \end{aligned} \tag{221}$$

$$\begin{aligned} E^{(0)} \frac{\partial^2 C_k^{c(2)}}{\partial E_i \partial E_j} = & - (\mu_i \frac{\partial C_k^{c(1)}}{\partial E_j} + \mu_j \frac{\partial C_k^{c(1)}}{\partial E_i}) - \alpha_{ij} C_k^{c(0)} \\ & \langle {}^{c}_{k} | x_j | {}^{d}_{l} \rangle \frac{\partial C_l^{d(1)}}{\partial E_i} + \langle {}^{c}_{k} | x_i | {}^{d}_{l} \rangle \frac{\partial C_l^{d(1)}}{\partial E_j} + \\ & \{ \langle {}^{c}_{k} | H | {}^{d}_{l} \rangle + \langle {}^{c}_{k} | H | {}^{d}_{l} \; 1 \rangle \} \frac{\partial^2 C_l^{d(2)}}{\partial E_i \partial E_j} \end{aligned} \tag{222}$$

Results and Discussion

All calculations were performed using INDO/S Model Hamiltonian [81, 82 101] with a minimum basis set All electric dipole moment results are in Debye. All polarizabilities results are in Å^3

The CI-SD, CI SDT, CI F and the reduced expanded space results (NEXP) were obtained by interpolating seven points to a third order polynomial

$$W(E) = W_0 + \mu E + \frac{\alpha}{2}E^2 + \frac{\beta}{6}E^3 \qquad (223)$$

The electric field strengths were 0, ±.001 a.u., ±.002 a.u., ±.003 a.u. for the principal axis of the molecule, and 0, ±.01 a.u., ±.02 a.u. ±.03 a u for the other directions. The mean square deviation was ± 10^{-7}.

In tables 12–15 we present the results for the Modified CI-S (MCI-S) obtained from equations 219–221. Modified CI-S without triples (MCI-S_WT) i e without the terms $\langle{}^{s}_{k}|H|{}^{t}_{l},1\rangle$ in equations 219–221. We also present the NEXP results obtained from applying the variational principle to a wave function of the form

$$|\psi\rangle = |0\rangle + C_1|1\rangle + C^{a}_{k}|{}^{a}_{k}\rangle \qquad (224)$$

where $|1\rangle = R_{RS}V|0\rangle$ and $|{}^{a}_{k}\rangle = \frac{1}{\sqrt{2}}(a^{\dagger}_{a}t_{\alpha} + a^{\dagger}_{\beta}t_{\beta})|0\rangle$. The polarizabilities are obtaining by interpolation as described above for CI.

We compare these results with Hartree-Fock, RPA, CI-S, CI SD, CI SDT and CI-F for water, carbon monoxide, formaldehyde and acethylene.

By Hartree-Fock we refer to a sum over states formula with Møller-Plesset energy denominators. CI-S is also a sum over states approach with the sum over diagonal states. Both might be considered as approximations to the RPA theory which is the full response of the Hartree-Fock wavefunction to an external perturbation. CI-SD, CI-SDT, CI F and NEXP are the full response of these wavefunctions to the external field. The MCI results discussed below are approximations to the CI-F results, as are, in a real sense, all the results reported.

From the polarizabilities results we see that CI-SD yields better results than CI-SDT, except in field directions which perpendicular to the plane of the molecule. This is also followed by our MCI results. Although the overall error between MCI-S and MCI-S_WT are about the same ±10%, the MCI S_WT seems to describe all directions better than MCI S. The NEXP results closely follows CI-SD in all cases.

RPA also performs remarkably well. This is due the very balanced way in which single and double excitations are included. However, for acethylene, the errors for the different directions of the fields (table 15) is 15% for the parallel direction and only 2% in the perpendicular directions while MCI-S_WT yields a 10% for the parallel direcoon and only 9% in the perpendicular directions, which are almost constant error.

From the dipole moment results, CI-SD also seems to outperform CI-SDT but in a less dramatic fashion. This is followed by our MCI-S and MCI-S_WT. The average error for CI-SD is 4%, for CI-SDT is 5%, for MCI-S is 10% and MCI S_WT is 15%.

In conclusion, it seems to be more accurate to use RPA or CI-SD than CI-SDT for reliable polarizabilities. MCI S_WT is a very promising method because it yields polarizabilities within ±10% of the CI-F results and it is an N^4 method where N is the number of the basis functions used, once the integral transforms are done. In this framework the NEXP method is competitive with CI-SD, since this method goes with N^5, while CI-SD dependence is N^6

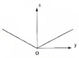

Table 12 Dipole Moment and Polarizability for water
d_{HO}=1.0081 Å θ_{HOH}=104.52° E_{HF}= 18 121337 Hartrees

Method	μ (Debyes)	α_{xx} (Å^3)	α_{yy} (Å^3)	α_{zz} (Å^3)
Hartree-Fock	2 2212 (4%)	0361 (59%)	3910 (34%)	2157 (9%)
CI S		0911 (3%)	- 6718 (13%)	-.2979 (25%)
RPA		0845 (4%)	6191 (4%)	.2471 (4%)
CI-SD	2 1437 (08%)	0883 (0%)	.5945 (02%)	.2364 (4%)
CI-SDT	2 1440 (1%)	-.0881 (.2%)	5945 (02)	2187 (8%)
NEXF	2 1484 (3%)	- 0882 (1%)	.5924 (3%)	2258 (5%)
MCI-S	2 2003 (3%)	.0867 (2%)	6363 (7%)	- 2723 (15%)
MCI S_WT	2.2008 (3%)	0840 (5%)	- 6290 (6%)	.2661 (12%)
CI-F	2 1419	- 0883	.5944	-.2374

Table 13 Polarizability for Carbon monoxide.
d_{CO}=1.12819 Å , E_{HF}= 22.619953 Hartrees

Method	μ (Debyes)	$\alpha_{//}$ (Å^3)	$\alpha_{\perp}$ (Å^3)
Hartree Fock	.0104 (98%)	1.9071 (33%)	-.4358 (47%)
CI-S		2.0491 (43%)	-.9467 (15%)
RPA		1.4455 (1%)	-.8318 (0.8%)
CI-SD	-.5246 (11%)	1.4713 (3%)	-.8263 (.1%)
CI SDT	.5142 (13%)	1.3866 (3%)	.8269 (.2%)
NEXT	-.5130 (13%)	1.4289 (0%)	-.8197 (.6%)
MCI-S	.4679 (20%)	1.7436 (22%)	.8263 (0.1%)
MCI S_WT	.3887 (34%)	-1.4629 (2%)	.7255 (12%)
CI F	.5892	1.4289	-.8251

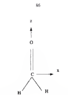

Table 14 Polarizability for formaldehyde d_{HC}=1.1020 Å d_{CO}=1.2100 Å θ_{HCH}=121.1° E_{HF}= 24.446548 Hartrees

Method	μ (Debyes)	α_{xx} (Å^3)	α_{yy} (Å^3)	α_{zz} (Å^3)
Hartree-Fock	2.2396 (14%)	3879 (21%)	2499 (45%)	1.4456 (28%)
CI-S		.5423 (10%)	4615 (8%)	2.0238 (79%)
RPA		- 4845 (2%)	4458 (3%)	-1.5922 (41%)
CI-SD	1.9669 (2%)	4883 (1%)	4571 (2%)	1.1326 (0%)
CI-SDT	-1.9942 (2%)	4934 (.06%)	4571 (2%)	-1.1784 (4%)
NEXP	2.0037 (2%)	4913 (.5%)	- 4513 (1%)	1.2278 (8%)
MCI-S	2.1053 (7%)	5130 (4%)	.4221 (8%)	-1.6353 (44%)
MCI S_WT	2.1228 (8%)	- 4730 (4%)	3925 (14%)	-1.4516 (28%)
CI F	1.9627	4937	.4580	1.1326

Table 15 Polarizability for acetylene, d_{HC}=1.0600 Å d_{CC}=1.2030 Å E_{HF}=-13.574985 Hartrees

Method	$\alpha_{//}$ (Å^3)	$\alpha_{\perp}$ (Å^3)
Hartree-Fock	-2.5676 (35%)	-.2298 (34%)
CI-S	-2.9991 (58%)	-.3643 (5%)
RPA	-2.1753 (15%)	-.3427 (2%)
CI SD	-1.9193 (1%)	-.3452 (5%)
CI SDT	-1.9546 (3%)	-.3471 (3%)
NEXP	-2.0040 (6%)	-.3460 (.6%)
MCI-S	-2.4709 (30%)	.3401 (2%)
MCI-S WT	-2.0703 (9%)	-.3141 (10%)
CI-F	-1.8982	-.3480

CHAPTER 5
REDUCED EXPANDED SPACE METHOD APPLIED TO ELECTRONIC SPECTROSCOPY

Introduction

Foresman, Head-Gordon, Pople and Frisch [102] divide electronic structure theories for excited-states chemistry into two types:

1. Those methods which concentrate on the physics of the transition, e.g. Random Phase Approximation [57, 65, 103, 104], and other Green Function methods [57, 65, 105, 106].
2. Those methods which concentrate on the physics of the state, e.g. SCF-CI, MCSCF, GVB, SAC-CI.

They also suggested a general criteria for an acceptable theoretical model for excited states:

> *The most satisfactory theoretical model chemistry will be one which is well-defined, applicable to systems of interest, size-consistent, and variational. Turning specifically to excited states, there is an additional desideratum. A given theoretical framework should lead to accurate representations of several electronic states, and these should have wave functions which are directly comparable. This qualification*

is necessary in order to calculate transition properties among the various possible states. It also ensures the ability to quantify the differences between the structure of the excited and ground states..

In this chapter we investigate an approximate scheme that tries to fulfill all of Pople's criteria with the exception of size-consistency, while trying to incorporate the physics of the state and the transition. Also, we keep strong ties with TDA, which allows for an easy interpretation of the spectra.

In section 2, we describe our method for excited states. In section 3, we present results for some selected systems: water, formaldehyde, and acetylene. Finally, in section 4, we present a summary and our conclusions.

Reduced Expanded Space Method applied to excited states

The lowest level of theory to yield excitation energies, transition moments and wave functions is single excitation configuration interaction (CI-S), or the Tamm Dancoff approximation (TDA). This approximation consists in using the orbitals of a HF state in an ordinary CI procedure and solving for higher roots. Excited determinants are produced by replacing one occupied orbital by a virtual orbital. Considering the simplicity of this approximation, the results are quite remarkable. One generally obtains the right order of the low lying transitions and fairly good transition energies, however, the transition moments are often exaggerated. One can greatly improve the transition moments by the inclusion of double excitation to the manifold (CI SD), however this usually makes the transition energies worse due to the strong coupling between the ground state with the double excited state manifold which is not balanced with respect to the single excited states. Sometimes the inclusion of double excitations even reverse the correct order of the states. The inclusion of triple excitations, specially those which double excitations with respect to the single excited state, corrects this by lowering the energies of the single excited states. Schematically,

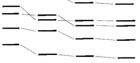

Figure 12. Typical behavior of CI state energies with the increase of the excitation manifold

RPA [103] usually gives good transition energies and transition moments. This accomplished by a careful inclusion of some double excitations. However one looses the description of states In fact, one can interpret the RPA as if each excited state had a ground state especially derived to insure the calculation of good oscillator strengths

So, one concludes that in the chemistry of excited states, it is desirable to include correlation in order to obtain reliable transition moments However, it must be included in a balanced fashion, i.e. all states should be correlated at the "same level" to avoid distortions, as occur, for example in such procedures as CI SD

In many cases, the correlation present in the ground state and in the excited states are very similar In such cases one can apply single excitations to a reference function optimized for the ground state and obtain a good approximation of a correlated excited state One can say that the correlation is portable This is the idea behind SAC CI [1–18] which has proven quite successful And it also confirms the observation of Öhrn and co-workers [100] that RPA and TDA on an antisymmetric geminal power reference function yields similar results

We propose, for a closed shell Hartree-Fock reference function ($|0\rangle$), a mul-tielectron basis set of the form

$$\{|0\rangle, \{|^{a}_{i}\rangle\}, \{|^{ab}_{ij}\rangle\}, \{|N\rangle\}, \{|^{a}_{i}\ N\rangle\}\} \qquad (225)$$

explicitly

$|^{a}_{i}\rangle = a^{\dagger}_{i}|0\rangle$ are the single excited configurations.

$|^{cd}_{kl}\rangle = c^\dagger d^\dagger lk|0\rangle$ are some specific double excited configurations,

$|N\rangle = \frac{1}{(E_o-H_o)^N}QV|0\rangle, \quad N = 1, N_{max}$ are the functions which represents the double excited configurations manifold not explicitly included

The triple excitations are included in a similar fashion to the double excitations We express this in two different ways the first,

$$|^{a}_{i}, N\rangle = \frac{1}{(E_o - H_o)^N} Qa^\dagger i QV|0\rangle, \quad N = 1, N_{max} \tag{226}$$

has a denominator which is the sum of the orbital energies of three holes minus the sum of the orbital energies of three particles, while the second

$$|^{a}_{i}, N\rangle = a^\dagger i Q \frac{1}{(E_o - H_o)^N} QV|0\rangle, \quad N = 1, N_{max} \tag{227}$$

is a single excitation on the "average" double excited functions

where

$$\begin{gathered} \hat{Q} = \hat{1} - \left(|0\rangle\langle 0| - |^{a}_{i}\rangle\langle^{a}_{i}| - |^{cd}_{kl}\rangle\langle^{cd}_{kl}|^{*}\right) \\ P + Q = 1 \end{gathered} \tag{228}$$

$$H = H_o + V \tag{229}$$

$$H_o = f_{pq} p^\dagger q, \quad f_{pq} = \langle p| - \frac{1}{2}\nabla^2|q\rangle + \langle pk||qk\rangle \tag{230}$$

$$V = \frac{1}{4}\langle pq||rs\rangle p^\dagger q^\dagger sr - \langle pk||qk\rangle p^\dagger q \tag{231}$$

$$\langle pq||rs\rangle = \int \varphi_p^*(\mathbf{x_1})\varphi_q^*(\mathbf{x_2})\frac{(1-P_{12})}{r_{12}}\varphi_r(\mathbf{x_1})\varphi_s(\mathbf{x_2})\mathbf{dx_1dx_2} \tag{232}$$

$$|0\rangle \quad \langle 0|H|0\rangle = E_{HF} \tag{233}$$

$$E_0 = \langle 0|H_0|0\rangle = f_{kk} \tag{234}$$

$$\Lambda_{max} \leq 5 \tag{235}$$

Hence one has to solve a secular problem of the form

$$H'_{ij}C_j = E_{corr}\Delta_{ij}C_j \tag{236}$$

where

$$H' = H - \langle 0|H|0\rangle \tag{237}$$

$$E_{corr} = E - E_{HF} \tag{238}$$

$$|\psi\rangle = C_J|\psi_J\rangle \tag{239}$$

$$H'_{IJ} = \langle\psi_I|H'|\psi_J\rangle \tag{240}$$

$$\Delta_{IJ} = \langle\psi_I|\psi_J\rangle \tag{241}$$

Explicit expressions for the elements of matrix

If one neglects the terms in parenthesis in the average triples denominator, one gets the second formulation for the average triples.

Overlap. $\Delta_{IJ} = \langle\psi_I|\psi_J\rangle$

$$\langle 0|0\rangle = 1 \tag{242}$$

$$\langle 0|{}^{c}_{k}\rangle = 0 \tag{243}$$

$$\langle 0|{}^{cd}_{kl}\rangle = 0 \tag{244}$$

$$\langle 0 | N \rangle = 0 \tag{245}$$

$$\langle 0 | {}^{a}_{i} N \rangle = 0 \tag{246}$$

$$\langle {}^{b}_{j} | {}^{a}_{i} \rangle = \delta_{ij} \delta_{ab} \tag{247}$$

$$\langle {}^{b}_{j} | {}^{cd}_{kl} \rangle = 0 \tag{248}$$

$$\langle {}^{b}_{j} | N \rangle = 0 \tag{249}$$

$$\langle {}^{b}_{j} | {}^{a}_{i} N \rangle = 0 \tag{250}$$

$$\langle {}^{fg}_{mn} | {}^{cd}_{kl} \rangle = \frac{1}{4} (\delta_{fc} \delta_{gd} - \delta_{fd} \delta_{gc})(\delta_{mk} \delta_{nl} - \delta_{ml} \delta_{nk}) \tag{251}$$

$$\langle {}^{fg}_{mn} | N \rangle = 0 \tag{252}$$

$$\langle {}^{ij}_{ab} | {}^{a}_{i} N\rangle = 0 \tag{253}$$

$$\langle M|N\rangle = \frac{1}{4}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)^{M+N}} \tag{254}$$

$$\langle M | {}^{a}_{i} N\rangle = 0 \tag{255}$$

$$\begin{aligned}
&\langle {}^{b}_{j} M | {}^{a}_{i} N\rangle = \\
&\frac{\delta_{ab}\delta_{ij}}{4}\frac{\langle kl||cd\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^{M+N}} \\
&-\frac{\delta_{ab}}{2}\frac{\langle ki||cd\rangle\langle cd||kj\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^{M}(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^{N}} \\
&-\frac{\delta_{ij}}{2}\frac{\langle kl||ca\rangle\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^{M}(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^{N}} \\
&+\frac{\langle ki||ca\rangle\langle cb||kj\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^{M}(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^{N}}
\end{aligned} \tag{256}$$

Hamiltonian, $H' = H - \langle 0|H|0\rangle$

$$\langle 0|H'|0\rangle = 0 \tag{257}$$

$$\langle 0|H'|{}^{a}_{i}\rangle = f_{ia} = 0 \tag{258}$$

$$\langle 0|H'|^{cd}_{kl}\rangle = \langle kl||cd\rangle \tag{259}$$

$$\langle 0|H'|N\rangle = \frac{1}{4}\frac{\langle kl||cd\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d)^N} = \langle 1|N-1\rangle \tag{260}$$

$$\langle 0|H'|^a_i\, N\rangle = 0 \tag{261}$$

$$\langle^b_j|H'|^a_i\rangle = \delta_{ij}f_{ba} - \delta_{ab}f_{ij} + \langle ib||aj\rangle \tag{262}$$

$$\begin{aligned}
&\langle^b_j|H'|^{cd}_{kl}\rangle = \\
&+\delta_{jk}\langle bl||cd\rangle + \delta_{jl}\langle kb||cd\rangle \\
&-\delta_{bc}\langle kl||jd\rangle - \delta_{bd}\langle kl||cj\rangle
\end{aligned} \tag{263}$$

$$\begin{aligned}
&\langle^b_j|H'|N\rangle = \\
&+\frac{1}{2}\frac{\langle kb||cd\rangle\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d)^N} \\
&-\frac{1}{2}\frac{\langle kl||cj\rangle\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b)^N}
\end{aligned} \tag{264}$$

$$\langle^b_j|H'|^a_i\, N\rangle = \langle^b_j\, 0|^a_i\, N\rangle \tag{265}$$

$$
\begin{aligned}
&\langle {}^{fg}_{mn}|H'|{}^{cd}_{kl}\rangle = \\
&(\delta_{fc}f_{gd}-\delta_{fd}f_{gc}+\delta_{gd}f_{fc}-\delta_{gc}f_{fd})(\delta_{mk}\delta_{nl}-\delta_{ml}\delta_{nk})+ \\
&-(\delta_{mk}f_{ln}-\delta_{ml}f_{kn}+\delta_{nl}f_{km}-\delta_{nk}f_{lm})(\delta_{fc}\delta_{gd}-\delta_{fd}\delta_{gc})+ \\
&(\delta_{mk}\delta_{nl}-\delta_{ml}\delta_{nk})\langle fg||cd\rangle+(\delta_{fc}\delta_{gd}-\delta_{fd}\delta_{gc})\langle kl||mn\rangle+ \\
&\delta_{fd}[-\delta_{mk}\langle lg||cn\rangle+\delta_{ml}\langle kg||cn\rangle-\delta_{nl}\langle kg||cm\rangle+\delta_{nk}\langle lg||cm\rangle]+ \\
&\delta_{gd}[+\delta_{mk}\langle lf||cn\rangle-\delta_{ml}\langle kf||cn\rangle+\delta_{nl}\langle kf||cm\rangle-\delta_{nk}\langle lf||cm\rangle]+ \\
&\delta_{fc}[+\delta_{mk}\langle lg||dn\rangle-\delta_{ml}\langle kg||dn\rangle+\delta_{nl}\langle kg||dm\rangle-\delta_{nk}\langle lg||dm\rangle]+ \\
&\delta_{gc}[-\delta_{mk}\langle lf||dn\rangle+\delta_{ml}\langle kf||dn\rangle-\delta_{nl}\langle kf||dm\rangle+\delta_{nk}\langle lf||dm\rangle]
\end{aligned}
\tag{266}
$$

$$
\begin{aligned}
&\langle {}^{fg}_{mn}|H'|\Lambda\rangle = \\
&\frac{1}{2}\,\frac{\langle fg||cd\rangle\langle cd||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_d)^N}+\frac{1}{2}\,\frac{\langle kl||mn\rangle\langle fg||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_g)^N}+ \\
&+\frac{\langle kg||cn\rangle\langle cf||km\rangle}{(\varepsilon_k+\varepsilon_m-\varepsilon_c-\varepsilon_f)^N}-\frac{\langle kg||cm\rangle\langle cf||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_f)^N} \\
&-\frac{\langle kf||cn\rangle\langle cg||km\rangle}{(\varepsilon_k+\varepsilon_m-\varepsilon_c-\varepsilon_g)^N}+\frac{\langle kf||cm\rangle\langle cg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_g)^N}
\end{aligned}
\tag{267}
$$

$$\langle {}^{fg}_{mn}|H'|{}^{i}_{a}, N\rangle =$$

$$\begin{aligned}
&+\frac{\langle ig||ac\rangle\langle fc||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_f+(\varepsilon_i-\varepsilon_a))^N}+\frac{\langle fi||ca\rangle\langle cg||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\\
&-\delta_{af}\frac{1}{2}\frac{\langle ig||cd\rangle\langle cd||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}-\delta_{ag}\frac{1}{2}\frac{\langle fi||cd\rangle\langle cd||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&+\delta_{in}[\frac{\langle kg||ca\rangle\langle cf||km\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_f+(\varepsilon_i-\varepsilon_a))^N}-\frac{\langle fk||ac\rangle\langle cg||km\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}]\\
&+\delta_{im}[\frac{\langle fk||ac\rangle\langle cg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}-\frac{\langle kg||ca\rangle\langle fc||nk\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_f+(\varepsilon_i-\varepsilon_a))^N}]\\
&+\frac{\delta_{in}\delta_{ag}}{2}\frac{\langle kf||cd\rangle\langle cd||km\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{im}\delta_{af}}{2}\frac{\langle kg||cd\rangle\langle cd||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&-\frac{\delta_{in}\delta_{af}}{2}\frac{\langle kg||cd\rangle\langle cd||km\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}-\frac{\delta_{im}\delta_{ag}}{2}\frac{\langle kf||cd\rangle\langle cd||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}
\end{aligned} \tag{268}$$

$$-\frac{\langle ik||an\rangle\langle fg||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}-\frac{\langle ki||ma\rangle\langle fg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}$$

$$-\delta_{in}\frac{1}{2}\frac{\langle kl||ma\rangle\langle fg||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}-\delta_{im}\frac{1}{2}\frac{\langle kl||an\rangle\langle fg||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}$$

$$\begin{aligned}
&-\delta_{ag}[\frac{\langle ik||nc\rangle\langle fc||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}-\frac{\langle ik||mc\rangle\langle fc||nk\rangle}{(\varepsilon_n+\varepsilon_k-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}]\\
&-\delta_{af}[\frac{\langle ik||mc\rangle\langle gc||nk\rangle}{(\varepsilon_n+\varepsilon_k-\varepsilon_g-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}-\frac{\langle ik||nc\rangle\langle gc||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_g-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}]
\end{aligned}$$

$$-\frac{\delta_{ag}\delta_{in}}{2}\frac{\langle kl||cm\rangle\langle cf||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}-\frac{\delta_{af}\delta_{im}}{2}\frac{\langle kl||cn\rangle\langle cg||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}$$

$$+\frac{\delta_{ag}\delta_{im}}{2}\frac{\langle kl||cn\rangle\langle cf||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{gf}\delta_{ie}}{2}\frac{\langle kl||cm\rangle\langle cg||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_e))^N}$$

$$\begin{aligned}
&\langle N'|H'|N\rangle=-\langle N'-1|N\rangle\big(=\langle N'|N-1\rangle\big)+\\
&\frac{1}{8}\frac{\langle kl||fg\rangle\langle fg||cd\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_g)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d)^N}+\\
&\frac{1}{8}\frac{\langle mn||cd\rangle\langle kl||mn\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_d)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d)^N}+\\
&\frac{\langle ml||fd\rangle\langle fk||mc\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_l-\varepsilon_f-\varepsilon_d)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d)^N}
\end{aligned}\tag{274}$$

$$\begin{aligned}
&\langle N'|H'|_i^a\,N\rangle=\\
&+\frac{\langle ik||fc\rangle\langle fl||ad\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_f-\varepsilon_c)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&+\frac{1}{2}\frac{\langle ik||af\rangle\langle fl||cd\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_f-\varepsilon_a)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&+\frac{1}{2}\frac{\langle kl||fd\rangle\langle fi||ca\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_d)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&-\frac{1}{4}\frac{\langle kl||fa\rangle\langle fi||cd\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_f)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&-\frac{\langle mk||ac\rangle\langle il||md\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_a)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&-\frac{1}{2}\frac{\langle km||cd\rangle\langle il||am\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_d)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&-\frac{1}{2}\frac{\langle mi||ca\rangle\langle kl||md\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_m-\varepsilon_c-\varepsilon_a)^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}\\
&+\frac{1}{4}\frac{\langle mi||cd\rangle\langle kl||ma\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_i-\varepsilon_c-\varepsilon_d)^N\,(+\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}
\end{aligned}\tag{275}$$

$$\begin{aligned}\langle{}^{b}_{j},N'|H'|{}^{a}_{i},N\rangle &= \left[-\langle{}^{b}_{j},N'|{}^{a}_{i}(N-1)\rangle+\right] \\ &\left\{=-\langle{}^{b}_{j},N'|{}^{a}_{i}(N-1)\rangle-(\varepsilon_{i}-\varepsilon_{a})\langle{}^{b}_{j}N'|{}^{a}_{i}N\rangle\right\}+\end{aligned} \tag{276}$$

where the terms in braces are for the $|{}^{a}_{i},N\rangle = a^{\dagger}{}_{i}R^{N}V|0\rangle$ triples and the terms in brackets are for the $|{}^{a}_{i}N\rangle = R^{N}a^{\dagger}{}_{i}V|0\rangle$, above

$$\begin{aligned}\delta_{ab}\delta_{ij}\ (&\frac{1}{8}\frac{\langle kl||fg\rangle\langle fg||cd\rangle\langle cd||kl\rangle}{(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{f}-\varepsilon_{g}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{1}{8}\frac{\langle mn||cd\rangle\langle kl||mn\rangle\langle cd||kl\rangle}{(\varepsilon_{m}+\varepsilon_{n}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{\langle ml||fd\rangle\langle fk||mc\rangle\langle cd||kl\rangle}{(\varepsilon_{m}+\varepsilon_{l}-\varepsilon_{f}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}})+\end{aligned}$$

$$\begin{aligned}\delta_{ab}\ (&\frac{1}{4}\frac{\langle ik||fg\rangle\langle fg||cd\rangle\langle cd||kj\rangle}{(\varepsilon_{i}+\varepsilon_{k}-\varepsilon_{f}-\varepsilon_{g}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{j}+\varepsilon_{k}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{1}{2}\frac{\langle kl||fd\rangle\langle if||cj\rangle\langle cd||kl\rangle}{(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{d}-\varepsilon_{f}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{\langle il||fd\rangle\langle kf||cl\rangle\langle cd||kj\rangle}{(\varepsilon_{i}+\varepsilon_{l}-\varepsilon_{f}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{j}+\varepsilon_{k}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{\langle li||fd\rangle\langle kf||cj\rangle\langle cd||kl\rangle}{(\varepsilon_{i}+\varepsilon_{l}-\varepsilon_{f}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{\langle kl||cd\rangle\langle ci||kf\rangle\langle fd||lj\rangle}{(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{j}+\varepsilon_{l}-\varepsilon_{f}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+ \\ &\frac{1}{2}\frac{\langle km||cd\rangle\langle li||mj\rangle\langle cd||kl\rangle}{(\varepsilon_{k}+\varepsilon_{m}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{j}-\varepsilon_{b}))^{N}(\varepsilon_{k}+\varepsilon_{l}-\varepsilon_{c}-\varepsilon_{d}+(\varepsilon_{i}-\varepsilon_{a}))^{N}}+\end{aligned}$$

$$-\frac{1}{4}\frac{\langle kl||cd\rangle\langle im||kl\rangle\langle cd||jm\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_m-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{1}{4}\frac{\langle im||cd\rangle\langle kl||jm\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_m-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N})+$$

$$\delta_{ij}\ (\frac{1}{4}\frac{\langle cb||kl\rangle\langle kl||mn\rangle\langle mn||ac\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_a-\varepsilon_c+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+$$
$$\frac{1}{2}\frac{\langle bk||ma\rangle\langle ml||cd\rangle\langle cd||kl\rangle}{(\varepsilon_l+\varepsilon_m-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{\langle kd||cm\rangle\langle ml||da\rangle\langle cb||kl\rangle}{(\varepsilon_l+\varepsilon_m-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{\langle ml||ad\rangle\langle kb||cm\rangle\langle cd||kl\rangle}{(\varepsilon_m+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{\langle kl||cd\rangle\langle cm||ka\rangle\langle bd||ml\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_m+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$\frac{1}{2}\frac{\langle kl||cf\rangle\langle bf||ad\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{1}{4}\frac{\langle kl||af\rangle\langle bf||cd\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{1}{4}\frac{\langle kl||cd\rangle\langle cd||af\rangle\langle bf||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_f+(\varepsilon_i-\varepsilon_a))^N})+$$

$$+\frac{\langle ik||fc\rangle\langle bf||da\rangle\langle cd||kj\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$+\frac{1}{2}\frac{\langle ki||cd\rangle\langle cd||fa\rangle\langle bf||jk\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_k-\varepsilon_b-\varepsilon_f+(\varepsilon_i-\varepsilon_a))^N}+$$
$$+\frac{1}{2}\frac{\langle ik||af\rangle\langle fb||cd\rangle\langle cd||kj\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_a-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$

$$
\begin{aligned}
&+\frac{\langle km||ca\rangle\langle li||jm\rangle\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_m-\varepsilon_a-\varepsilon_c+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\\
&+\frac{1}{2}\frac{\langle im||ac\rangle\langle kl||mj\rangle\langle cb||kl\rangle}{(\varepsilon_i+\varepsilon_m-\varepsilon_a-\varepsilon_c+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\\
&+\frac{1}{2}\frac{\langle kl||ca\rangle\langle im||kl\rangle\langle cb||jm\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_c+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_m-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{4}\frac{\langle kl||cd\rangle\langle ib||aj\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+\\
&-\frac{1}{2}\frac{\langle il||cd\rangle\langle kb||al\rangle\langle cd||kj\rangle}{(\varepsilon_i+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+\\
&+\frac{1}{2}\frac{\langle kl||ad\rangle\langle id||cj\rangle\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\\
&+\frac{\langle li||da\rangle\langle kd||cl\rangle\langle cb||kj\rangle}{(\varepsilon_i+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_k-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2}\frac{\langle kl||cd\rangle\langle ib||ak\rangle\langle cd||jl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_j+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+\\
&-\frac{1}{2}\frac{\langle il||cd\rangle\langle kb||aj\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2}\frac{\langle kl||ad\rangle\langle ib||cj\rangle\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+\\
&-\frac{1}{2}\frac{\langle kl||cd\rangle\langle ci||ja\rangle\langle bd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+
\end{aligned}
$$

$$-\frac{\langle kl||ca\rangle\langle ic||dk\rangle\langle db||lj\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_c+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_j+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{\langle il||ad\rangle\langle dk||jc\rangle\langle cb||kl\rangle}{(\varepsilon_i+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+$$

$$-\frac{\langle li||da\rangle\langle kb||cl\rangle\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$-\frac{\langle ki||cd\rangle\langle cl||ka\rangle\langle bd||jl\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$

$$+\frac{\langle kl||ad\rangle\langle ib||cl\rangle\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_j+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$+\frac{\langle ki||cd\rangle\langle cl||ja\rangle\langle bd||kl\rangle}{(\varepsilon_i+\varepsilon_k-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$

$$+\frac{\langle li||da\rangle\langle kb||cj\rangle\langle cd||kl\rangle}{(\varepsilon_i+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}+$$
$$+\frac{\langle kl||cd\rangle\langle ci||ka\rangle\langle db||lj\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N\,(\varepsilon_j+\varepsilon_l-\varepsilon_b-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$

Dipole Moment Matrix Elements

$$\langle\chi|\vec{r}|\psi\rangle = \langle\chi|x|\psi\rangle\vec{e}_x + \langle\chi|y|\psi\rangle\vec{e}_y + \langle\chi|z|\psi\rangle\vec{e}_z$$

$$\begin{aligned}
&\langle 0|x|0\rangle = \langle k|x|k\rangle = x_{kk}\\
&\langle 0|x|{}^{a}_{i}\rangle = \langle i|x|a\rangle = x_{ia}\\
&\langle 0|x|{}^{cd}_{kl}\rangle = 0\\
&\langle 0|x|N\rangle = 0\\
&\langle 0|x|{}^{a}_{i}\ N\rangle = 0
\end{aligned} \tag{289}$$

$$\langle 0|x|{}^{a}_{i}\rangle = \langle i|x|a\rangle = x_{ia} \tag{290}$$

$$\langle 0|x|{}^{cd}_{kl}\rangle = 0 \tag{291}$$

$$\langle 0|x|N\rangle = 0 \tag{292}$$

$$\langle 0|x|{}^{a}_{i}\ N\rangle = 0 \tag{293}$$

$$\langle {}^{b}_{j}|x|{}^{a}_{i}\rangle = \delta_{ij}\delta_{ab}\langle 0|x|0\rangle + \delta_{ij}\langle b|x|a\rangle - \delta_{ab}\langle i|x|j\rangle \tag{294}$$

$$\begin{aligned}
\langle {}^{b}_{j}|x|{}^{cd}_{kl}\rangle &= \delta_{bc}\delta_{jk}\langle l|x|d\rangle + \delta_{bd}\delta_{jl}\langle k|x|c\rangle\\
&- \delta_{bc}\delta_{jl}\langle k|x|d\rangle - \delta_{bd}\delta_{jk}\langle l|x|c\rangle
\end{aligned} \tag{295}$$

$$\langle{}^{b}_{j}|x|N\rangle = \frac{\langle cb||kj\rangle}{(\varepsilon_k + \varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}})^N}\langle k|x|c\rangle \tag{296}$$

$$\langle{}^{b}_{j}|x|{}^{a}_{i}, N\rangle = 0 \tag{297}$$

$$\begin{aligned}\langle{}^{fg}_{\mathbf{mn}}|x|{}^{cd}_{kl}\rangle = {} & (\delta_{fc}\delta_{gd} - \delta_{fd}\delta_{gc})(\delta_{\mathbf{mk}}\delta_{\mathbf{n}l} - \delta_{ml}\delta_{\mathbf{nk}})\langle 0|x|0\rangle \\ & + (\delta_{\mathbf{mk}}\delta_{\mathbf{n}l} - \delta_{ml}\delta_{\mathbf{nk}})[\delta_{fc}\langle g|x|d\rangle + \delta_{gd}\langle f|x|c\rangle + \\ & \qquad - \delta_{fd}\langle g|x|c\rangle - \delta_{gc}\langle f|x|d\rangle] \\ & - (\delta_{fc}\delta_{gd} - \delta_{fd}\delta_{gc})[\delta_{\mathbf{mk}}\langle l|x|n\rangle + \delta_{\mathbf{n}l}\langle k|x|m\rangle + \\ & \qquad - \delta_{\mathbf{m}l}\langle k|x|n\rangle - \delta_{\mathbf{nk}}\langle l|x|m\rangle]\end{aligned} \tag{298}$$

$$\begin{aligned}\langle{}^{fg}_{mn}\langle x|N\rangle = {} & \frac{\langle cg||mn\rangle}{(\varepsilon_m + \varepsilon_n - \varepsilon_c - \varepsilon_g)^N}\langle f|x|c\rangle + \frac{\langle fc||mn\rangle}{(\varepsilon_m + \varepsilon_n - \varepsilon_c - \varepsilon_f)^N}\langle g|x|c\rangle \\ & - \frac{\langle fg||kn\rangle}{(\varepsilon_k + \varepsilon_n - \varepsilon_f - \varepsilon_g)^N}\langle k|x|m\rangle - \frac{\langle fg||mk\rangle}{(\varepsilon_m + \varepsilon_k - \varepsilon_f - \varepsilon_g)^N}\langle k|x|n\rangle\end{aligned} \tag{299}$$

$$\begin{aligned}
\langle {}^{fg}_{mn}|x|^{a}_{i}, N\rangle &= \frac{\langle fg||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\langle i|x|a\rangle \\
&-\left\{\frac{\delta_{in}\,\langle fg||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{im}\,\langle fg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\right\}\langle k|x|a\rangle \\
&-\left\{\frac{\delta_{ag}\,\langle fc||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{af}\,\langle cg||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\right\}\langle i|x|c\rangle \\
&+\left\{\frac{\delta_{in}\delta_{ag}\,\langle fc||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{im}\delta_{af}\,\langle cg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\right\}\langle k|x|c\rangle \\
&-\left\{\frac{\delta_{im}\delta_{ag}\,\langle fc||nk\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}+\frac{\delta_{in}\delta_{af}\,\langle cg||km\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_c-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N}\right\}\langle k|x|c\rangle
\end{aligned} \tag{300}$$

$$\begin{aligned}
\langle N'|x|N\rangle &= \langle N'|N\rangle\,\langle 0|x|0\rangle \\
&+\frac{1}{2}\,\frac{\langle mn||fg\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_g)^N}\,\langle f|x|c\rangle\,\frac{\langle cg||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_c-\varepsilon_g)^N} \\
&-\frac{1}{2}\,\frac{\langle mn||fg\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_g)^N}\,\langle k|x|m\rangle\,\frac{\langle fg||kn\rangle}{(\varepsilon_k+\varepsilon_n-\varepsilon_f-\varepsilon_g)^N}
\end{aligned} \tag{301}$$

$$\begin{aligned}
\langle N'|x|^{a}_{i}\, N\rangle &= \frac{1}{4}\,\frac{\langle mn||fg\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_g)^N}\,\langle i|x|a\rangle\,\frac{\langle fg||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N} \\
&-\frac{1}{2}\,\frac{\langle mi||fg\rangle}{(\varepsilon_m+\varepsilon_i-\varepsilon_f-\varepsilon_g)^N}\,\langle k|x|a\rangle\,\frac{\langle fg||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_g+(\varepsilon_i-\varepsilon_a))^N} \\
&-\frac{1}{2}\,\frac{\langle mn||fa\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_a)^N}\,\langle i|x|c\rangle\,\frac{\langle fc||mn\rangle}{(\varepsilon_m+\varepsilon_n-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N} \\
&+\frac{\langle mi||fa\rangle}{(\varepsilon_m+\varepsilon_i-\varepsilon_f-\varepsilon_a)^N}\,\langle k|x|c\rangle\,\frac{\langle fc||mk\rangle}{(\varepsilon_m+\varepsilon_k-\varepsilon_f-\varepsilon_c+(\varepsilon_i-\varepsilon_a))^N}
\end{aligned} \tag{302}$$

$$\langle {}^{b}_{j}, N' | x | {}^{a}_{i}, N \rangle = \langle {}^{b}_{j}, N' | {}^{a}_{i}, N \rangle \langle 0 | x | 0 \rangle + \tag{303}$$

$$\delta_{ab}\delta_{ij}[-\frac{1}{2}\frac{\langle ml||cd\rangle}{(\varepsilon_m+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle k|x|m\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle kl||fd\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle f|x|c\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}]+$$

$$\delta_{ab}[-\frac{1}{4}\frac{\langle kl||cd\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle i|x|j\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle ki||cd\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle l|x|j\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle kl||cd\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle i|x|l\rangle\frac{\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle li||cd\rangle}{(\varepsilon_l+\varepsilon_i-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle k|x|l\rangle\frac{\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$-\frac{\langle ki||cf\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N}\langle f|x|d\rangle\frac{\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}]+ \tag{305}$$

$$-\delta_{ij}[-\frac{1}{4}\frac{\langle kl||cd\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle b|x|a\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle kl||ad\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle b|x|c\rangle\frac{\langle cd||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle kl||cf\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_f+(\varepsilon_j-\varepsilon_b))^N}\langle f|x|a\rangle\frac{\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{1}{2}\frac{\langle kl||fa\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_f-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle f|x|c\rangle\frac{\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$-\frac{\langle ml||ca\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle k|x|m\rangle\frac{\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}]+$$

$$+\frac{1}{2}\frac{\langle kl||ca\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle i|x|j\rangle\frac{\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$-\frac{1}{2}\frac{\langle ki||cd\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle b|x|a\rangle\frac{\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$
$$-\frac{\langle li||ca\rangle}{(\varepsilon_l+\varepsilon_i-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle k|x|l\rangle\frac{\langle cb||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{\langle ki||da\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_a-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle d|x|c\rangle\frac{\langle cb||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}+$$

$$-\frac{\langle ki||ca\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle l|x|j\rangle\frac{\langle cb||kl\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$-\frac{\langle kl||ca\rangle}{(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle i|x|l\rangle\frac{\langle cb||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{\langle ki||cd\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_d+(\varepsilon_j-\varepsilon_b))^N}\langle d|x|a\rangle\frac{\langle cb||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_b+(\varepsilon_i-\varepsilon_a))^N}$$
$$+\frac{\langle ki||ca\rangle}{(\varepsilon_k+\varepsilon_i-\varepsilon_c-\varepsilon_a+(\varepsilon_j-\varepsilon_b))^N}\langle b|x|d\rangle\frac{\langle cd||kj\rangle}{(\varepsilon_k+\varepsilon_j-\varepsilon_c-\varepsilon_d+(\varepsilon_i-\varepsilon_a))^N}$$

A great simplification can be achieved if spin adaptation is included. then one would obtain a multi-electron basis set for singlets

1. $\{|0\rangle \{|^a_i\rangle\} \{|^{cd}_{kl}\rangle\}, \{|N\rangle\}, \{|^a_i N\rangle\}\}$
2. $|^a_i\rangle = S_i^{a\dagger}|0\rangle \quad S_i^{a\dagger} = \frac{1}{\sqrt{2}}(a_{\alpha}^{\dagger} i_{\alpha} + a_{\beta}^{\dagger} i_{\beta})$
3. $|^{cd}_{kl}\rangle = S_k^{c\dagger} S_l^{d\dagger}|0\rangle$
4. $|N\rangle = \frac{1}{(E_0-H_0)^N} QV|0\rangle \quad N = 1, M$
5. a $|^a_i N\rangle = \frac{1}{(E_0-H_0)^N} QS_i^{a\dagger}QV|0\rangle \quad N = 1, M$

b. $|^{a}_{i}, N\rangle = Q S_{i}^{a\dagger} \frac{1}{(E_0-H_0)^N} QV|0\rangle, \quad N = 1, M$

6 $Q = \hat{1} - (|0\rangle\langle 0| - |^{a}_{i}\rangle\langle^{a}_{i}| - |^{cd}_{kl}\rangle\langle^{cd}_{kl}|)$

Results

All calculations were performed using INDO/S Model Hamiltonian [81, 82, 101] with minimum basis set.

In the tables 17 to 22 we present the transition energies and oscillator strengths for water, formaldehyde and acetylene. We compare our variational results (see table 16) with CI-S, CI-SD, CI-SDT and CI-F.

Table 16 Description of the NEXP basis sets used

Method	Multielectron Basis
NEXP1-S	$\{\|0\rangle, RV\|0\rangle, \{\|^{a}_{i}\rangle\}\}$
NEXP1-ST_1	$\{\|0\rangle, RV\|0\rangle, \{\|^{a}_{i}\rangle\}, \{Ra^{\dagger}_{i}V\|0\rangle\}\}$
NEXP1-ST_0	$\{\|0\rangle, RV\|0\rangle, \{\|^{a}_{i}\rangle\}, \{a^{\dagger}_{i}RV\|0\rangle\}\}$
NEXP1-ST_1 + doubles (i,j)=>(a,b)	$\{\|0\rangle, RV\|0\rangle, \{\|^{a}_{i}\rangle\}, \{Ra^{\dagger}_{i}QV\|0\rangle\}, \{\|^{fg}_{mn}\rangle\}\}$ $a \le f \le g \le b,\ i \le m \le j\ \ i \le n \le j$
NEXP1-ST_0 + doubles (i,j)=>(a,b)	$\{\|0\rangle, RV\|0\rangle, \{\|^{a}_{i}\rangle\}, \{a^{\dagger}_{i}RV\|0\rangle\}, \{\|^{fg}_{mn}\rangle\}\}$ $a \le f \le g \le b,\ i \le m \le j\ \ i \le n \le j$

Clearly, in all cases CI-SDT gives results very close to the CI-F results. CI-S also performs quite well giving the right order of the states except for acetylene. CI-SD greatly improves the transition moments and yields better oscillator strengths.

NEXP1–S presents the same trends as CI-S, except with larger transition energies, a consequence of the fact that $RV|0\rangle$ correlates the ground state. This is partly corrected by the inclusion of average triple excitations. The explicit inclusion of some selected double excitations yields, in general, to the worst qualitative results; e.g. we note an intruder state problem for NEXP1–ST_0 + doubles (4 6)=>(7 8) in formaldehyde and an inversion of states for NEXP-ST_1 + doubles (4 6)=>(7,8), again in the case of formaldehyde.

For acetylene, NEXP1–ST_0 gives the same ordering of the states as the CI-SDT for the first three transitions. This is quite remarkable because there is a change in symmetry from Π to Σ in transitions two, three and four. This is not destroyed by the inclusion of double excitations, although it is not sufficient to correct the order of the fourth transition (Σ_g). The NEXP1–ST_1 scheme is related closely to NEXP1–S and consequently to CI-S. NEXP1–S presents the same ordering as CI-S, and the inclusion of triples changes the nature of the fourth transition from Π_g to Σ_g, this result is not altered by the inclusion of the selected double excited states.

For acetylene, the inclusion of triples results in better agreement with CI SDT. The NEXP1–ST_0 scheme scheme also performs better for the first three transitions of formaldehyde. This suggests that the single excited states are not very sensitive to the relative weight of the triple excitations.

In summary, the NEXP spectroscopic methods presented here really do not perform as well as we had hoped although for most systems they are quite good for the first few transitions. CI-S and CI-SDT are good theories for the lowest lying states, although CI-SDT becomes prohibitively expensive.

Table 17 Excitation Energies and Oscillator Strengths for water d_{HO}=1.0081 Å θ_{HOH}=104.52°, E_{HF}=-18.121337 Hartrees

	Ground State Depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
CI-S	0.0	80996.9 (.0279) B_1 (3%)	87098.6 (f.b.s) A_2 (4%)	102918.5 (.0117) A_1 (1%)	111174.3 (.1777) B_2 (1%)
CI-SD	-.038157	81916.0 (.0245) B_1 (4%)	87628.9 (f.b.s) A_2 (5%)	104888.8 (.0078) A_1 (3%)	112742.5 (.1560) B_2 (3%)
CI-SDT	-.038220	78710.1 (.0254) B_1 (.2%)	83916.9 (f.b.s) A_2 (.2%)	101981.9 (.0095) A_1 (.08%)	109902.6 (.1604) B_2 (.07%)
CI-F	-.038616	78574.7 (.0231) B_1	83761.6 (f.b.s) A_2	101897.3 (.0096) A_1	109822.8 (.1529) B_2

Table 18. Excitation Energies and Oscillator Strengths for water, d_{HO}=1.0081 Å, θ_{HOH}=104.52°, E_{HF}=-18.121337 Hartrees

	Ground State Depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
NEXP1-S	-.037561	89241.8 (.0290) B_1 (14%)	95343.5 (f.b.s) A_2 (14%)	111156.8 (.0081) A_1 (9%)	119419.6 (.1796) B_2 (9%)
NEXP1-ST_0	-.037582	85290.0 (.0281) B_1 (8%)	91184.7 (f.b.s) A_2 (9%)	107904.0 (.0106) A_1 (6%)	116434.0 (.1779) B_2 (6%)
NEXP1-ST_1	-.037613	85332.6 (.0269) B_1 (9%)	91245.1 (f.b.s) A_2 (9%)	107909.0 (.0093) A_1 (6%)	116506.5 (.1759) B_2 (6%)
CI-F	-.038616	78574.7 (.0231) B_1	83761.6 (f.b.s) A_2	101897.3 (.0096) A_1	109822.8 (.1529) B_2

Table 19 Excitation Energies and Oscillator Strengths for formaldehyde, d_{HC}=1.1020 Å, d_{CO}=1.2100 Å, θ_{HCH}=121.1°, E_{HF}=-24.446548 Hartrees

	Ground State depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
CI-S	0.0	20205.5 (f.b.s) A_2 (11%)	55015.5 (.0176) B_2 (6%)	75466.4 (.3074) A_1 (11%)	97291.3 (.0000) B_1 (24%)
CI-SD	-.102306	26276.3 (f.b.s) A_2 (44%)	65732.6 (.0153) B_2 (13%)	85556.4 (.0071) A_1 (25%)	85845.3 (.0032) B_1 (9%)
CI-SDT	-.102996	17474.6 A_2 (4%)	66101.8 B_2 (13%)	72462.1 A_1 (6%)	78110.4 B_1 (6%)
CI-F	-.107694	18213.8 A_2	58254.5 B_2	68240.8 A_1	78592.5 B_1

Table 20 Excitation Energies and Oscillator Strengths for formaldehyde, d_{HC}=1.1020 Å, d_{CO}=1.2100 Å, θ_{HCH}=121.1°, E_{HF}=-24.446548 Hartrees.

	Ground State depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
NEXP1-S	-.096747	41439.5 (f.b.s) A_2 (127%)	76248.9 (.0241) B_2 (31%)	96584.9 (.2467) A_1 [illegible] (41%)	118373.4 (.0000) B_1 (50%)
NEXP1-ST_0	-.096983	29812.1 (f.b.s) A_2 (64%)	66523.1 (.0216) B_2 (14%)	86962.8 (.2710) A_1 (27%)	102814.6 (.0001) B_1 (31%)
NEXP1-ST_1	-.097924	30127.4 (f.b.s) A_2 (65%)	66799.7 (.0209) B_2 (15%)	86161.8 (.2128) A_1 (26%)	103533.4 (.0002) B_1 (32%)
NEXP1 ST_0 +doubles (4,6)=>(7,8)	-.101832	27556.0 (f.b.s) A_2 (51%)	64504.9 (.0223) B_2 (11%)	85309.5 (.1595) A_1 (25%)	86286.1 (f.b.s) A_2
NEXP1-ST_1+ doubles (4,6)=>(7,8)	-.104624	12460.9 (f.b.s) A_2 (32%)	55384.8 (.0201) B_2 (5%)	68186.4 (.0041) B_1 (13%)	80088.0 (.0376) A_1 (17%)
CI-F	-.107694	18213.8 A_2	58254.5 B_2	68240.8 A_1	78592.5 B_1

Table 21 Excitation Energies and Oscillator Strengths for acetylene d_{HC}=1.0600 Å, d_{CC}=1.2030 Å, E_{HF}=-13.574985 Hartrees

	Ground State depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
CI S	0.0	49023.3 (.0000) Σ_u (20%)	53388.3 (.0000) Δ_u (19%)	90473.3 (f.b.s) Π_g (3%)	110378.5 (.0867) Π_u
CI-SD	-.102757	71575.7 (.0000) Σ_u (17%)	75507.8 (.0000) Δ_u (15%)	101609.7 (f.b.s) Π_g (9%)	112353.1 (f.b.s) Σ_g (6%)
CI-SDT	-.102940	60346.3 Σ_u (1%)	65019.3 Δ_u (1%)	92009.9 Π_g (2%)	111934.2 Σ_g (6%)
CI-F	-.110520	61234.7 Σ_u	65822.9 Δ_u	93527.4 Π_g	105955.8 Σ_g

Table 22 Excitation Energies and Oscillator Strengths for acetylene, d_{HC}=1 0600 Å, d_{CC}=1.2030 Å, E_{HF}=-13.574985 Hartrees

	Ground State depression (Hartrees)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)	Transition Energy (cm^{-1}) (Oscilator Strength) Excited State (Error)
NEXP1 S	097614	70448 1 (0000) Σ_u (15%)	74813 1 (0000) Δ_u (14%)	111898 6 (f b s) Π_g (20%)	131804 0 (0930) Π_u
NEXP1 ST_0	097641	58966 0 (0000) Σ_u (4%)	64534 7 (0000) Δ_u (2%)	98296 8 (f b.s) Π_g (5%)	106947 1 (0000) Σ_u
NEXP1 ST_1	097683	59134 4 (0000) Σ_u (3%)	64056 9 (0000) Δ_u (3%)	98629 1 (f b.s) Π_g (5%)	107772 6 (4531) Σ_u
NEXP1 ST_0+ doubles (4,5)=>(6.7	099007	59265 9 (0000) Σ_u (3%)	64834 7 (0000) (0032) Δ_u (1%)	98596 7 (f b.s) Π_g (5%)	107247 0 (0000) Σ_u
NEXP1 ST_1+ doubles (4,5)=>(6.7	099046	59433.6 (.0000) Σ_u (3%)	64356 1 (0000) (0029) Δ_u (2%)	98928.3 (f b.s) Π_g (6%)	108071.8 (.5977) Σ_u
CI F	- 110520	61234 7 Σ_u	65822 9 Δ_u	93527.4 Π_g	105955.8 Σ_g

CHAPTER 6
SUMMARY AND CONCLUSIONS

In chapter 3, we analyze a Krylov-like expansion which, although it can be generalized, we use to expand the double-excited states. The variational energy obtained by using the basis set $\{|0\rangle, \{R_{RS}^{n}V|0\rangle\}\}$ is stable at all internuclear distances and captures over 95% of the correlation energy obtained by CI-D. This is particularly interesting since our method is an N^5 method, while CI-D is N^6, where N is the number of basis functions. We also showed the connection of these functions to the first order Brillouin Wigner Perturbation Theory wavefunction. This analysis suggested an effective non-iterative method to obtain the Brillouin-Wigner energies, a method which converges quickly when the HOMO-LUMO gap is even modest. Our non-iterative method of solving Brillouin-Wigner Perturbation Theory differs from that of Bartlett and Brändas [19–23] in the choice of the functions used. The method of Bartlett and Brändas functions depends on element of matrix of positive powers of the Hamiltonian, while our functions depends on positive powers of the Rayleigh-Schroedinger resolvent.

In chapter 4, we obtain an N^4 method for polarizabilities that yields good results when compared with CI-F. This method, called Modified CI-S Without Triples (MCI-S_WT), seems particularly suitable to applications for large systems

In chapter 5, we present two ways to account for triple excitations. Both methods seem to balance the average inclusion of double excitations, resulting in rather good transition moments (±10% error with respect to CIF), and in a good description of the low lying transitions.

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BIOGRAPHICAL SKETCH

Monique Revorêdo Chacon was born to Leda Maria Revorêdo and Luis Chacon in Recife, Brazil, on November 10, 1960. She is the eldest of three children.

She lived in Recife until she came to Gainesville, Florida. At age of five, she started kindergarten and elementary school at Colégio Santa Maria in Recife. At age of eleven, she changed school to Colégio das Damas da Instrução Cristã where she stayed for four years. Then she started high school again at Colégio Santa Maria leaving again one year later to spend two years at Colégio Contacto where she concluded high school. She obtained her Bacharelado em Física at the Universidade Federal de Pernambuco in December, 1982. She went on to obtain her Mestrado em Física again at the Universidade Federal de Pernambuco in January, 1985. In August, 1985 she came to the University of Florida.

Monique's interest in science started early while using her father's small telescope to see the stars. In high school, her interest changed to chemistry making her decide to start university as a chemical engineering major. After two years of university, she was very disappointed and ready to drop out of school and go around the world in a boat when Dr. Arnóbio Gama offered her the opportunity of a physics undergraduate fellowship with Dr. Sylvio Canuto, who eventually became her master's supervisor.

She still is interested in other scientific fields, and has flirted with the idea of switching to cosmology, field theory, oceanography, scientific journalism, and, more recently, enviromental and biological sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences, and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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